Computational approaches to study adsorption in MOFs with unsaturated metal sites

Michael Fischer[1], José R. B. Gomes[2], Miguel Jorge[3*]

1) *UCL Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom*

2) *CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal*

3) *Department of Chemical and Process Engineering, University of Strathclyde, 75 Montrose Street, Glasgow G1 1XJ, United Kingdom*

*corresponding author email: miguel.jorge@strath.ac.uk

Computational approaches to study adsorption in MOFs with unsaturated metal sites

Metal-organic frameworks with coordinatively unsaturated sites (CUS) offer interesting possibilities for tuning the affinity of these materials towards certain adsorbates, potentially increasing their selectivity and storage capacity. From a modelling point of view, however, they pose a significant challenge due to the inability of conventional force-fields for dealing with these specific interactions. In this paper, we review recent developments in the application of quantum-mechanical methods and classical molecular simulations to understand and predict adsorption in MOFs with CUS. We find that hybrid approaches that incorporate QM-based information into classical models are able to provide dramatically improved adsorption predictions relative to conventional force-fields, while yielding a realistic description of the adsorption mechanism in these materials.

Keywords: Monte Carlo simulation; density functional theory; adsorption; MOFs; open metal sites; multiscale modelling

1. Introduction

Metal-organic frameworks (MOFs) are a group of crystalline materials consisting of inorganic building units that are connected by organic linker molecules [1,2, 3].While the simplest possible inorganic building unit is an isolated metal cation, polynuclear metal-oxygen clusters are more typical. MOFs with coordinatively unsaturated metal sites (CUS, sometimes also referred to as “open” metal sites), are a particularly interesting group of MOFs. In these systems, at least one available coordination site of the metal centre is occupied by an atom belonging to a solvent molecule after the synthesis. Through activation using evacuation, heat, or solvent exchange, the solvent molecules can be removed, leaving the metal atom “undercoordinated”. The differences between an as-synthesised MOF and an activated system are visualised for the example of MOF-74 in Figure 1. The CUS can act as sites of specific interaction with guest

molecules, and therefore have a beneficial impact on various properties. For example, metal-hydrogen interactions lead to an increased heat of hydrogen adsorption, which is beneficial for hydrogen storage applications [4]. Other potential applications for these systems lie in the field of gas separation, where the increased interaction of one species with the metal site can enhance the separation efficiency [5], and in catalysis, where metal sites may act as Lewis acid sites [6].

While the first reported MOF with CUS was Zn(bdc), with bdc = 1,4-benzenedicarboxylate, which was synthesised in 1998 by Yaghi and co-workers [7], the earliest system that has received continued attention was presented the following year [8]: This MOF, often dubbed HKUST-1 or CuBTC, has the stoichiometry $Cu_3(btc)_2$, with btc = 1,3,5-benzenetricarboxylate. The structure consists of Cu_2 paddle-wheels connected by the tripodal btc linkers. After solvent removal, each copper centre has one free coordination site. Later on, analogous systems with other metals have been prepared, and a comparative study of gas adsorption in these $M_3(btc)_2$ systems was reported recently [9]. The members of the MOF-74 series are another group of MOFs with accessible metal sites that have been studied intensely for various applications. Zn-MOF-74 was first published in 2005 [10], and isostructural systems with other metal centres have been presented subsequently. These systems, which are sometimes referred to as M_2(dobdc), M_2(dhtp), or CPO-27, consist of one-dimensional chains of five-coordinated metal centres, connected by 2,5-dioxido-1,4-benzenedicarboxylate linkers (Figure 1). Comparative studies of MOF-74 analogues with different metals have been reported with regard to H_2 [11], CH_4 [12], and CO_2 adsorption [13]. Through replacement of the linker by molecules that contain chains of up to 11 phenylene rings, Yaghi and co-workers were able to synthesise a MOF with CUS and very large pores with diameters of up to 98 Å [14].

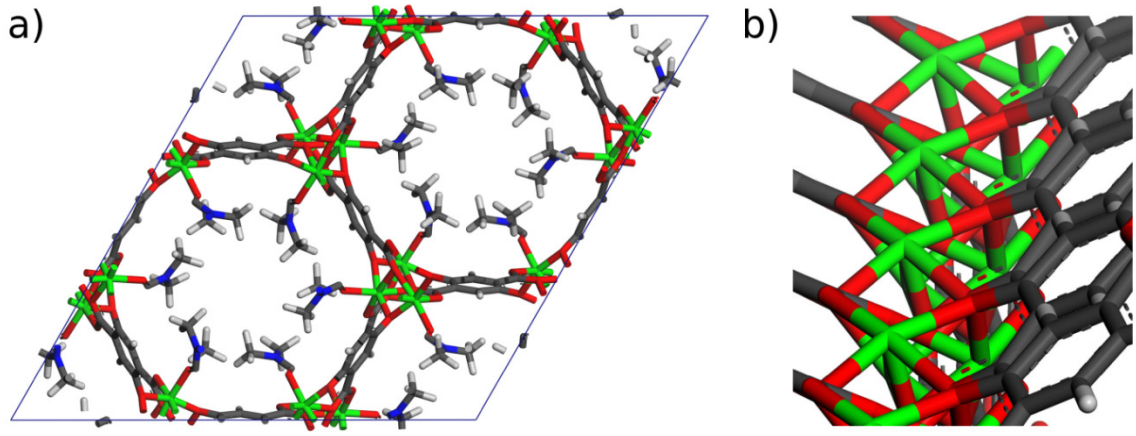

Figure 1: *a) Visualisation of the structure of as-synthesised Zn-MOF-74, with DMF molecules coordinated to the metal sites [10]. B) Detailed view of the coordinatively unsaturated metal sites of Zn-MOF-74 after removal of the coordinated solvent molecules.*

Although it can be hypothesised from adsorption experiments that a preferential adsorption of guest molecules at the CUS occurs, e.g., on the basis of higher isosteric heats of adsorption, this method provides no direct evidence. A direct localisation of the molecules in the pores is possible using diffraction experiments. While the determination of the position of strongly coordinated molecules, such as water or other solvents, is relatively easy to achieve using X-ray diffraction, the localisation of weakly adsorbed species requires a more elaborate setup: In these *in-situ* experiments, a MOF sample is loaded with a well-defined amount of gas and then cooled down to very low temperatures (typically 20 K or less) before the diffraction experiment is carried out. In most cases, neutron radiation is used, as this facilitates the detection of guest molecules with relatively few electrons. The first report of an in-situ diffraction study of a system with CUS was published in 2006 by Peterson *et al.* [15]: These authors investigated the adsorption of deuterium in CuBTC (D_2, rather than H_2, is used in neutron diffraction

experiments to avoid the incoherent scattering of the ^{1}H nuclei). It was found that adsorption at low partial pressures occurs primarily at the copper sites, with a Cu-D_2 distance of 2.4 Å. This distance lies significantly below the sum of the van der Waals radii of Cu and H_2. Other adsorption sites are occupied subsequently. Similar diffraction studies were carried out later for the same MOF and CD_4 [16], C_2D_2 [17], and CO_2 [18], to name just a few guest species of particular relevance. In addition to CuBTC, other MOFs incorporating CUS were investigated in this context, such as members of the MOF-74 series [12, 18, 19], the charged-framework $(M_4Cl)_3(btt)_8$ systems [20, 21], as well as a set of structurally different MOFs with Cu_2 paddle-wheel units [22].

More indirect evidence for the localised interaction with metal sites can be inferred using IR spectroscopy. This was demonstrated as early as 2006 by Bordiga and co-workers, who studied the adsorption of H_2 and CO in CuBTC using *in-situ* IR spectroscopy [23]. For both molecules, a significant shift of characteristic bands of the guest species was observed, indicating a localised interaction with the copper sites. Other spectroscopic studies have addressed the adsorption of H_2 in different MOF-74 analogues [24], as well as the Lewis acidity of MIL-100(Al) [25]. In the latter case, *in-situ* IR spectroscopy experiments were performed with three different probe molecules (CO, pyridine, CD_3CN) to achieve a thorough characterisation of the system. Quite frequently, IR spectroscopic methods have been combined with density-functional theory (DFT) calculations, e.g., in a study of CO_2, CO, and N_2 in MOF-74 [26].

Furthermore, solid-state NMR spectroscopy has been found to provide valuable insights into the interaction of guest species with CUS. This method was used by Haouas *et al.* [27] to investigate the activation of MIL-100(Al), who showed that the loss of water molecules coordinated to the metal sites is directly visible in the NMR

spectra. Very recently, NMR spectroscopy has also been used to probe the structure and dynamics of CO_2 adsorbed at the CUS of Mg-MOF-74 [28, 29].

This very brief summary, which is not meant to be exhaustive, shows how different experimental techniques can be exploited to characterise the adsorption at CUS, and also illustrates how important these effects are to understand adsorption in MOFs. Consideration of specific interactions between adsorbate molecules and CUS poses an interesting challenge for the modelling community. In this review, we discuss the application of computational chemistry methods to investigate the adsorption of different guest molecules at coordinatively unsaturated metal sites in MOFs. Important fundamental insight into these systems can be obtained by applying quantum-mechanical (QM) methods, and this is the focus of the first part of this review. The second part of the review focuses on force-field based grand-canonical Monte Carlo simulations. We start by discussing how approaches using standard force-fields often fail in describing adsorption at CUS, and then present different approaches to remedy this shortcoming, ranging from empirical "tuning" of selected force-field parameters to more sophisticated methods that combine QM with molecular simulation.

2. Quantum-mechanical methods

2.1. Molecular models

The extended structures of metal organic frameworks have been modelled with two different strategies, namely, the cluster model and the periodic cell approaches. The former relies on a finite number of atoms, centred at a region of interest (Figure 2). The selection of the cluster, i.e., its shape and the number of constituting atoms, is a very important step in any computational study since it will have direct consequences on the

quality of the final results. A small model, where dangling bonds are saturated by hydrogen atoms, enables the application of high-level computational approaches and large atomic centred basis sets, but the electronic environment of the atoms in the cluster will be severely affected by spurious effects related to the limited size of the model. This can be obviated by considering larger clusters, which will require a concomitant reduction of the quality of the computational approach, or by embedding the small model in a region of surrounding atoms that are treated with a low-level computational approach, e.g., by considering the $Cu_2(btc)_4$ cluster model in Figure 2 where the central atoms (copper and carboxylate groups) are treated with a high-level approach and the rest of the atoms are treated with a low-level approach. In the limit, we would like to end up with a portion of the material (small model) surrounded by an embedding region of infinite size.

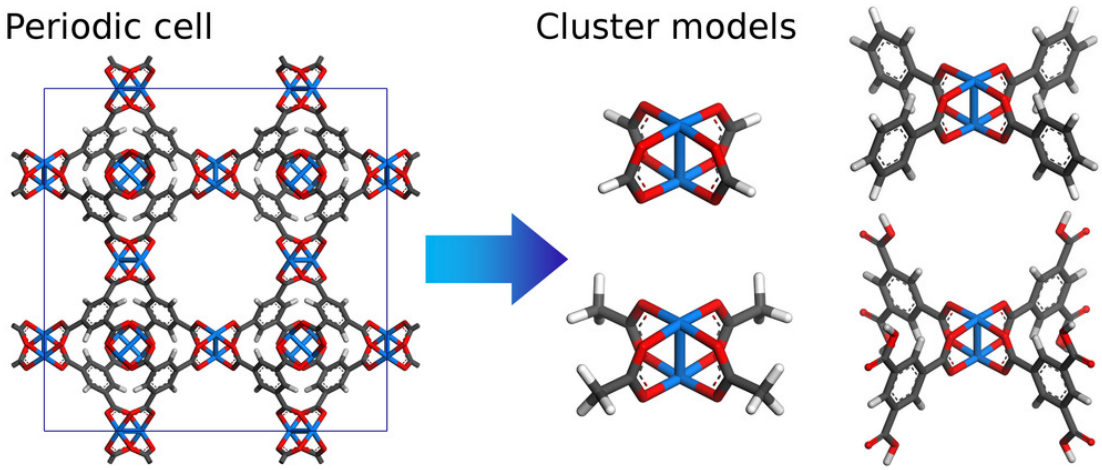

Figure 2. *Periodic cell (left) and four different sized cluster models (right) suitable to represent the CuBTC framework. In the cluster models, the copper dimer is bonded to four formate (top left), to four acetate (bottom left), to four benzoate (top right), or to four 1,3,5-benzenetricarboxylate (bottom right) linkers.*

The periodic cell approach is based on a repetition of a suitable unit cell in the three spatial dimensions (Figure 2). The problems caused by the finite size of the system associated with the cluster model approach are absent in the periodic approach. However, since most of the quantum-mechanical studies employing periodically repeated cells consider plane-wave basis sets, the selection of the unit cell is very critical when dealing with MOFs, since the empty space in the very large pores is included in the calculation in such situations.

In the case of MOFs presenting CUS, the uncertainties associated with the sizes and shapes of the models used are usually smaller than those resulting from the computational approaches considered, as will be shown below.

2.2. Basis sets

Quantum-mechanical studies relying on the cluster model approach often make use of basis sets of atom-centred basis functions to represent all the electrons of each atom in the molecular system. In modern practice, these atom-centred basis functions are usually chosen to be Gaussian-type orbitals (GTOs) since they are easier to calculate when compared, for instance, with Slater-type orbitals (STOs). Note that it is also possible to use GTOs with the periodic cell approach as in the case of the CRYSTAL code [30]. For example, cluster and periodic model studies based on GTOs were reported for the interaction of CO, CO_2 and N_2 with Mg-MOF-74 [26,31]. The quality of the calculations is intrinsically dependent on the number and shape of the functions that are used to describe each atomic orbital. Usually, the larger the basis set, the better the quality of the results coming from the calculation, with obvious implications in the computational resources required for the execution of the calculations. Clever ideas for saving computational resources include the consideration of several functions only for the valence shell electrons, which are those involved in bond making / bond breaking,

the so-called split-valence basis sets, which are the most used in QM studies, and the use of an effective core potential (ECP) to describe the core electrons (pseudopotential approach). The consideration of basis functions for each atom in the molecular system leads to the basis set superposition error (BSSE), which – as the name indicates – arises from the overlap of the basis functions of the atoms in interacting molecules (or even between different parts of the same molecule), leading to the overestimation of the intermolecular energies. This is a very important issue in the field of MOFs since several gaseous molecules, e.g., H_2 and CO_2, weakly interact with the framework and significant relative errors may arise for the calculated interaction energies if the BSSE is not corrected, for instance, by extrapolation to the complete basis set (CBS) limit or by the use of the counterpoise method. In the case of the extrapolation to the CBS limit, the Dunning's correlation consistent basis sets with or without diffuse functions, named aug-cc-pVXZ or cc-pVXZ, respectively, of X-zeta quality [32,33] are frequently used to eliminate the inaccuracies caused by the BSSE.

The BSSE problems are eliminated if plane-wave basis sets are used to describe the atoms in the system. This is the case in most studies using periodic models. Nevertheless, in the field of MOFs, it is possible to find some studies where fragments of the periodic crystalline structure of MOFs (instead of periodic models) were used together with the plane-wave approach [34, 35]. Note that the calculations are still based on the repetition of a unit cell but in such situations the cluster of atoms is surrounded by a vacuum region in order to avoid the interaction with the atoms in the surrounding cells. This is a very important point in the field of MOFs since dispersion forces have a noticeable role in the gas-MOF interaction, and large vacuum regions are needed in order to obtain reliable energetic data.

In summary, all the approaches described above have advantages and drawbacks. Possibly due to such reasons, some authors performed studies where periodic and cluster models, and GTOs or plane-waves basis sets, were combined to tackle the interaction of small gaseous molecules with MOFs [36,37, 38].

2.3. Computational approaches

Wave function and density functional theory (DFT) methods have been used in the past years to study MOFs but, as in other fields, DFT approaches are the most used due to a much more effective ratio between the quality of the calculated data and the computational resources required, and due to a much easier implementation in plane-wave codes than the former methods, which are usually employed to obtain benchmark data. The description of the interaction between gaseous molecules, such as H_2 or CO_2, and MOFs is quite challenging since standard DFT approaches based on the local density approximation (LDA) or on the generalised-gradient approximation (GGA) cannot correctly describe the van der Waals attractive tail [39]. However, such approaches seem to appropriately treat the Pauli repulsion and the short range attraction felt by the adsorbate in regions close to the minima in the potential energy surface (PES), and despite yielding quantitatively wrong interaction energies, they can reproduce well the trend of experimental energies of interaction [11] and may be used for comparison purposes. Note that such approaches have to be used with caution when the aim is the development of potentials for classical simulations since LDA overestimates and GGA underestimates the calculated interaction energies [11,40]. The most used approaches without dispersion corrections are the Perdew-Zunger (PZ, LDA type) [41] and the Perdew-Burke-Ernzerhof (PBE, GGA type) functionals [42, 43]. Interestingly, the PW91 and the PBE functionals were found to provide quite similar results for CO_2 adsorption on different metal MOF-74 [44], which is in line with

conclusions taken from previous work devoted to the study of molecular adsorption on metal surfaces [45].

Very recently, several different strategies were suggested for the inclusion of the van der Waals interactions in DFT approaches, ranging from quite simple empirical terms added to the DFT energy, which are based on dispersion coefficients for atom pairs, to more elaborate approaches where some components of the DFT exchange or correlation are substituted by other corrected terms or by fitting a large number of parameters in semilocal or hybrid functionals with data sets including systems with dispersive interactions. For a very recent review on the topic, the reader is referred to ref. [39]. In the field of MOFs, the most used DFT approaches including dispersion interactions are DFT-D2, i.e., a standard DFT approach plus empirical corrections following Grimme's scheme [46], and vdW-DF [47]. The former approach is based on the addition of an empirical correction to the DFT energy based on atomic C_6 coefficients, while in the latter approach, the dispersion corrections are based on fragment densities written in terms of maximally localized Wannier functions obtained from the occupied Kohn–Sham orbitals. Note that in the original version of the empirical force-field of Grimme *et al.* [46], identical van der Waals C_6 interaction coefficients are used for all the elements in the series K-Zn, which is a quite drastic approximation with relevant influence in the calculations for MOFs containing elements in this series. It should be pointed out here that overestimation of the bond lengths is typical in vdW-DF calculations [48] but this DFT approach usually yields interaction energies that are in close agreement with experimental data, when available [49, 50]. Additionally, a very recent study from Canepa *et al.* [51] using the vdW-DF and the periodic model approaches reproduced the geometry of a secondary binding site for

CO_2 in MOF-74-Mg (Figure 1), where the molecule binds the carboxylate group of the linker, found by neutron diffraction experiments.

Other authors proposed quite elegant schemes to improve the quality of the DFT results for the interaction of molecules with MOFs by correcting the DFT energies with contributions arising from high-level post-Hartree-Fock approaches (Moller-Plesset or coupled-cluster methods) combined with very large basis sets and cluster models [38, 52, 53]. Unfortunately, this kind of strategy needs a previous calculation of the correction factors for the system under study since they are not transferable from one system to another.

Many MOFs are based on transition metals having unpaired electrons, which require careful theoretical treatment of the corresponding spin-states. In fact, calculations for Fe- and Ni-containing MOFs showed that their interactions with molecules such as H_2 or CO can be quite strong or quite weak depending on the metal spin-state [54, 55], with obvious implications in the conclusions and in the predictions arising from the calculations.

2.4. Quantum-mechanical studies of MOFs with CUS

A large number of research works employing first-principles approaches were dedicated to H_2 and CO_2 gases since MOFs are quite promising for hydrogen storage, a critical enabling technology for a Hydrogen Economy [56], and for the capture and sequestration of carbon resulting from the burning of fossil fuels, which is one of the greatest environmental concerns facing mankind [57]. Despite the small size of these molecules, the computation of their interactions with MOFs presenting CUS is quite challenging due to difficulties in the correct description of the dispersion interactions (see above) and to the large unit cells of MOFs. Nevertheless, QM studies dedicated to

MOFs were able to provide valuable information, i.e., they were used to confirm and to interpret experimental results when available, and to predict the properties of MOFs that have not been synthesised so far. A selection of some of those computational studies will be reviewed in the following subsections distinguished according to the use of cluster or periodic approaches to model the systems.

2.4.1. Cluster model studies

MOFs based on transition metal paddle-wheels bridged by carboxylate-based linkers have been synthesised for elements in the 3d period of the periodic table [8,58,59] and shown to present good adsorption properties. Recently, Bak *et al.* [34] performed a comparative study of the interactions between Sc to Zn CUS and two adsorbates, namely, H_2 and pyridine, taken as examples of weak and strong Lewis bases, respectively. Their calculations, based on the plane-wave PBE approach, considered cluster models built from transition metal dimers coordinated to the oxygen atoms of four formate or four benzoate (bc) linkers, yielding cluster models of the type $TM_2(HCOO)_4$ or $TM_2(bc)_4$, respectively (see Figure 2). The interaction energy corresponding to the adsorption of H_2 at the Cu site, one molecule each side of the paddle-wheel, was -8.7 kJ/mol per molecule, which is in satisfactory agreement with the variable temperature infrared (VTIR) spectroscopic enthalpy determined by Bordiga *et al.* [60] for H_2 on CuBTC (-10.1 ± 0.7 kJ/mol). Note that the minus sign used in this review for the interaction energies means favourable adsorption. The proximity between the experimental and the PBE interaction energies is nevertheless fortuitous since dispersion interactions are not included in this approach, and much larger deviations between experimental and computational results are expected for adsorbates binding more strongly to the copper sites in CuBTC as in the case of water. Grajciar *et al.* [52] studied the interaction of water with a $Cu_2(HCOO)_4$ cluster model and found that the

differences between the PBE and the experimental enthalpies was much larger both in absolute and in percentage. The PBE result for water interacting with CuBTC is -32.4 kJ/mol while the experimental enthalpy at T=313 K is -50.7 ± 2.9 kJ/mol. A benchmark interaction energy of -51.2 kJ/mol was calculated by the same authors with the single-reference coupled cluster method (explicitly considering single and double excitations and treating the effect of triple excitations at the perturbation theory level), CCSD(T), with extrapolation to the CBS limit. The comparison of the PBE results from Bak *et al.* [34] show that Co and Zn paddle-wheels will more strongly adsorb the hydrogen molecule than the other metals studied. The PBE interaction energies for those metals are nearly twice (~ -19 kJ/mol) the value calculated for Cu. In the case of Ni, the interaction energy is -11.6 kJ/mol, while for the other metals, the energies vary between ~ -4 and -6 kJ/mol. The lower energies were explained as being the effect of covalent bonding between the metals in the paddle-wheels (Sc to Cr series) and due to strong ferromagnetic coupling in the cases of Mn and Fe systems. As expected, the interaction energies with pyridine were much stronger, especially with Sc and Zn paddle-wheels. Another important result from the study of Bak *et al.* is that similar interaction energies and adsorbate-metal distances were obtained with the $TM_2(HCOO)_4$ and the $TM_2(bc)_4$ cluster models, suggesting that the gas-MOF interaction has a localised character. Similar conclusions have been taken from our recent study [61]. Using a PBE approach and a double zeta numerical basis set with polarisation functions, we investigated the interaction of ethylene with copper paddle-wheels with different sized carboxylate linkers, e.g., formate, benzoate (benzenecarboxylate), 1,4-benzene-dicarboxylate, and 1,3,5-benzenetricarboxylate (Figure 2), and showed that the size of the cluster model has a small influence on the quality of the QM results for this kind of MOF. However, the positioning and nature of the ligands may produce very large differences, as pointed

out in the GGA-BLYP study of Kosa *et al.* [62] on the interaction of H_2 with a Ni^{2+} analogue of a hybrid inorganic-organic framework material. In that study, the interaction energy was found to vary between -6 and -23 kJ/mol, depending on the geometrical arrangement of the ligands in a cluster with square pyramidal shape and formula $NiL_3L'_2$. This is a very relevant observation for force-field transferability between MOFs, and requires special attention.

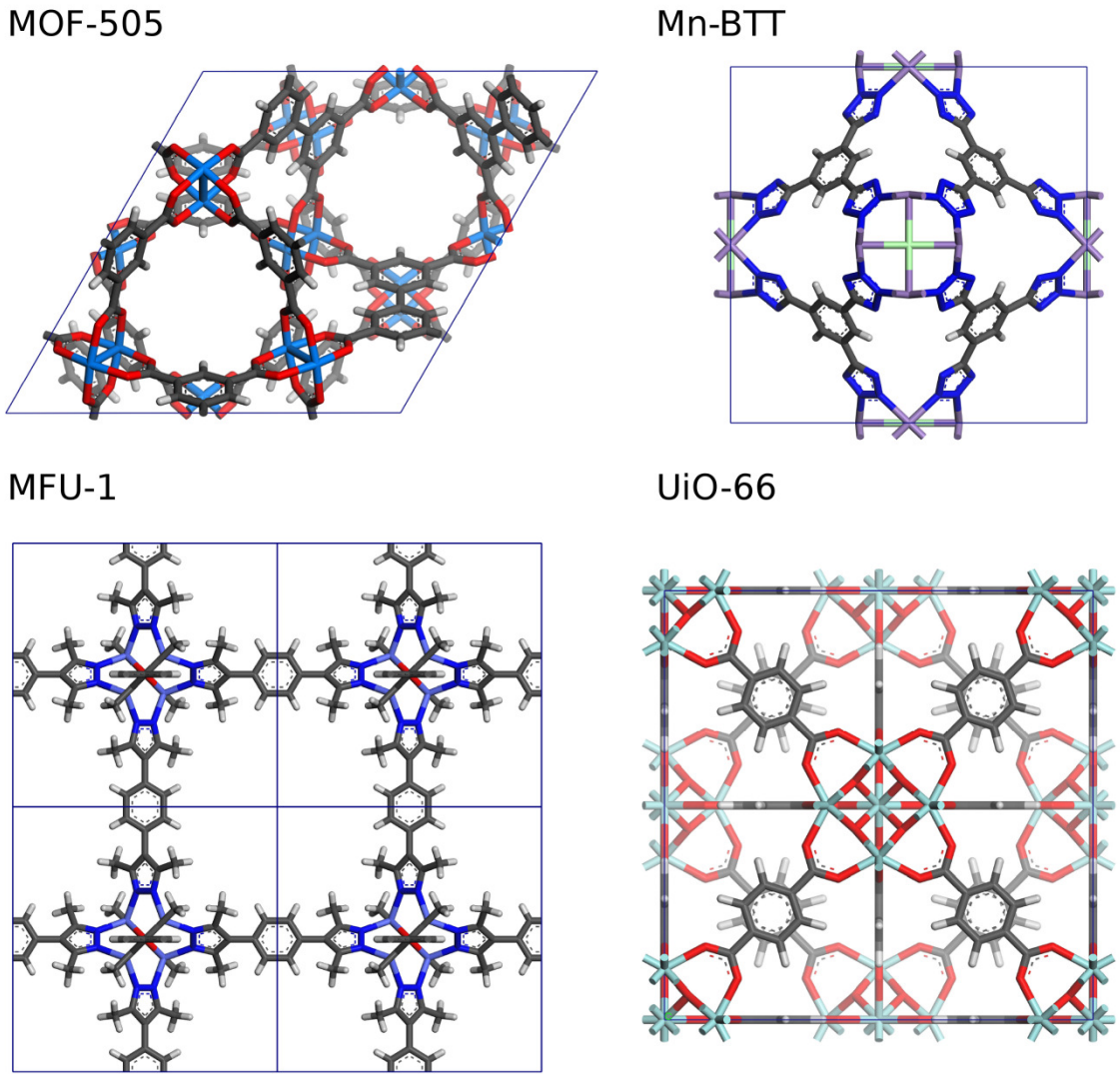

Figure 3. *Views of the crystallographic unit cells for MOF-505 (also referred to as* $Cu_2(bptc)$ *or NOTT-100),* $(Mn_4Cl)_3btt_8$ *(often abbreviated as Mn-BTT), MFU-1* $(Co_4O(bdpb)_2)$*, and UiO-66* $(Zr_6O_4(OH)_4(bdc)_6)$ *. The following abbreviations are used for the linker molecules: bptc = 3,3'-5,5'-biphenyltetracarboxylate, btt = 1,3,5-*

tris(tetrazolate-5-yl)benzene, bdpb =1,4-bis[(3,5-dimethyl)-pyrazolate-4-yl]benzene, bdc = 1,4-benzenedicarboxylate.

Another DFT study using a small cluster model for the Cu_2 paddle-wheel was performed by Fischer et al. [63,64]. In order to study the influence of substituents on the strength of the copper-hydrogen interaction, a variety of $Cu_2(L)_4$ clusters was investigated, with L being para-substituted benzoate ligands. It was found that electron-withdrawing substituents, such as nitro or cyano groups, lead to a significant increase of the interaction energy, whereas electron-donating substituents weaken the interaction. An analysis of the DFT electron density revealed a correlation of the interaction strength with the Hirshfeld charge at the Cu site, showing that the increase of the interaction energy is directly related to the increased positive polarisation of the metal site [64]. N-substituted ligands were found to have a similar effect as benzoate ligands with electron-withdrawing substituents. As the copper-hydrogen interaction is generally very weak, an analogous study was carried out with pyridine as a more strongly coordinating species. Again, the calculations revealed a drastic variation of the interaction strength as a function of the substituent. The interaction energy correlated well with both the Hirshfeld charge at the Cu site and the Hammett constant of the substituent [65]. There is a remarkable correspondence between these results and a combined experimental and theoretical study of the catalytic activity of a MOF by Vermoortele *et al.* [66]. In this work, it was shown that the reaction rate constant of a cyclisation reaction catalysed by UiO-66 materials with different substituted ligands correlates very well with the Hammett constant of the substituent. These findings show that the introduction of substituents can be used to significantly alter the electronic properties of the metal site, thereby influencing the adsorption behaviour and/or the

catalytic activity of the material. Theoretical studies using QM methods are a very valuable tool to predict and understand such effects.

Gomez and Sastre [67] studied the adsorption of H_2 on frozen cluster models of several MOFs, namely, Pd-MIL-88, Zr-UiO-66, V-MIL-47 and Co-MFU-1 (Figures 3 and 4) with wave function-based methods, e.g. MP2, and several GTO basis sets. They reported interaction energies ranging between -0.96 and -2.42 kJ/mol, considering saturation uptakes, which are in the range of the lower theoretical and experimental results for hydrogen adsorption on MOFs.

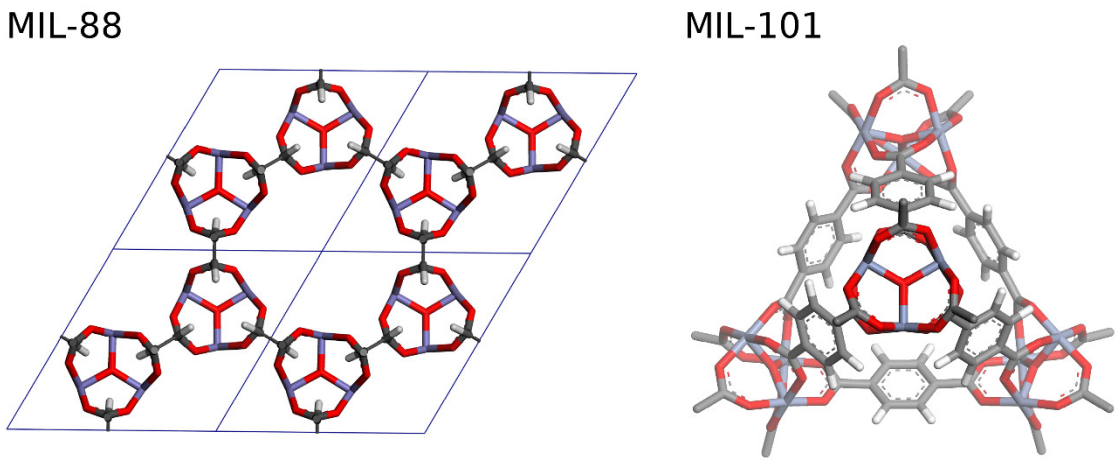

Figure 4. *Views of the structure of MIL-88 ($Fe_3O(fum)_6$) and of a tetrahedral fragment taken from the structure of MIL-101 ($Cr_3O(bdc)_3$). While all metal sites of the M_3O units are displayed as accessible in the plot, only some of the sites can be activated in the actual MOFs due to the coordination of charge-balancing anions (F^-, OH^-). Fum = fumarate.*

Sun *et al.* [35] studied the effect of the splitting and of the occupation of the spin orbitals of transition metal centres in MOFs on the strength of the H_2 binding to these materials using plane-wave PBE and cluster model approaches. The calculated energy

on a Mn-MOF cluster model was -8.4 kJ/mol at a distance of 2.42 Å from the metal centre. From the analysis of local density of states (LDOS) on Mn *d* and H *s* orbitals, these authors hypothesised that the small energy in Mn-based MOFs determined experimentally is caused by two competing mechanisms, i) an energy-gaining mechanism caused by the down-shift of bonding levels in the LDOS and ii) an energy-costing mechanism resulting from the up shift of occupied antibonding levels. They tested their hypothesis by performing new calculations where Mn was replaced by early transition metals. The latter possess a smaller number of electrons and therefore, the energy costing mechanism will be less important. In fact, much larger binding energies were obtained when Mn was replaced by Sc (-21.9 kJ/mol), Ti (-34.6 kJ/mol) and, especially, V (-46.5 kJ/mol), while the calculated energy for a Cu-MOF analogue was -4.4 kJ/mol.

A detailed analysis of the interaction between H_2 and the $Cu_2(bc)_4$ cluster model (Figure 2) was provided by Kim *et al.* [68] from a plane-wave PBE study. They found that the diatomic paddle-wheel configuration causes a strong localisation of the 4*s* orbital, which enables a σ-*s* coupling between the occupied $H_2\sigma$ and the unoccupied Cu^{2+} 4*s* orbitals, lowering the orbital energy of the occupied σ state. Based on these findings, they suggested that the coupling between the paddle-wheel and H_2 could be enhanced by addition of other *s*-orbital metals such as Zn and Mg. The calculations performed for CuZn or CuMg and Zn_2 or Mg_2 models confirmed the suggestions above, and the H_2 adsorption on the Zn and Mg sites was found to be 2–3 times stronger than that on Cu. This suggests a new direction in designing hydrogen storage materials.

The adsorption of other small molecules (CO, H_2O, N_2, O_2 and NO_x or SO_x and their hydrates) on MOFs was also studied by QM approaches due to their presence as impurities in flue gas mixtures, affecting the CO_2 capture by these materials. Yu *et al.*

considered cluster models of Mg-MOF-74 and MIL-101 (Figures 1 and 4), where only the atoms in the centre were optimised, to study the impact of these trace contaminants on the adsorption of CO_2 [31]. Their calculations considered the effects of dispersion interactions, using wB97XD and B3LYP-D2 approaches, and showed that the CUS, which are relevant for the enhanced uptake of CO_2 at low partial pressures shown by some MOFs, are poisoned by some of the trace contaminants considered in their study. The poisoning will be very effective in the case of the hydrates of SO_2 and SO_3, i.e., H_2SO_3 and H_2SO_4 species, respectively, for which the calculated binding enthalpies are much larger than the enthalpy of CO_2 interaction with the models of Mg-MOF-74 and MIL-101. A similar comparative study was performed by Ding and Yazaydin [69] but on the influence of SO_2, NO_2, NO, CO and O_2 in the CO_2 adsorption on several MOFs chosen as representative examples of materials containing high density of CUS per internal surface area (Mg-, Ni- and Co-MOF-74, Figure 1), of materials containing small pockets, large cages and CUS sites (CuBTC) and of materials with amine groups (BioMOF-11, and Zn-Atz-Ox, based on 3-amino-1,2,4-triazole and oxalic acid). Ding and Yazaydin found that SO_2 and NO are adsorbed ~5 and 3 times, respectively, more strongly than CO_2 on Mg-MOF-74, NO, NO_2 and O_2 adsorb more strongly than CO_2 on BioMOF-11, while all gases have similar interaction energies on Cu-BTC. This suggests that finding an ideal MOF for a specific application is quite a difficult task, and that the optimisation of computational techniques for screening purposes is very urgent. Interestingly, gas co-adsorption may have a beneficial effect on the CO_2 uptake, as illustrated by the calculations of Yu *et al.* [70] on CuBTC. The calculations without dispersion corrections (PBE approach) showed that the interaction of CO_2 with CuBTC with coordinated water is 4 kJ/mol higher (more negative) than that calculated for the interaction of CO_2 with the bare paddle-wheel. These observations were used by the

authors to propose a mechanism based on the competition for adsorption sites that explains the CO_2/N_2 selectivity demonstrated by CuBTC in the presence of uncoordinated water. At low pressures, water competes with N_2 to adsorb in the framework while CO_2 is stabilised by the presence of water, increasing the CO_2/N_2 selectivity, while at high pressure, competition between H_2O and CO_2 for the same adsorption sites becomes significant, i.e. the CO_2---water-material interaction is less important, which decreases the CO_2/N_2 selectivity. Very recently, Nijem et al. [71] suggested the co-adsorption of molecules in MOFs as a topic needing more attention from theoreticians (and experimentalists) due to their importance in the understanding of the diffusion and interactions of molecules in MOFs, which will lead to the design of better framework materials with enhanced properties. This is the main topic of a very recent study by Canepa et al. [51] that will be reviewed in the next sub-section.

In a very recent study, Verma *et al.* [72] studied the adsorption of C1-C3 hydrocabons, containing both saturated and unsaturated bonds, on Fe-MOF-74. They used the M06-L functional, which implicitly includes dispersion interactions and was previously validated for use with systems containing transition metals. Several cluster sizes, metal spin states and degrees of optimisation were considered in this investigation. Their results demonstrate that although dispersion interactions account for a significant fraction of the adsorption energies, all hydrocarbons show enhanced interactions with the CUS relative to what would be expected based on dispersion interactions alone. Importantly, interaction energies at the CUS are much stronger for unsaturated than for saturated hydrocarbons, in agreement with experimental observations [5]. The authors explained this enhancement based on a different adsorption mechanism – saturated hydrocarbons interact by weak electron donation from the σ-bonding orbital of the C-H bond to the 3*d*, 4*p* and 4*d* orbitals of Fe, while

unsaturated hydrocarbon bonding involves both donation from the π-bonding orbital of the C-C bond to the metal and back-donation from the filled d-orbitals of the metal to the unsaturated hydrocarbon, resulting in a much stronger binding energy. This work shows the potential of MOFs with CUS for hydrocarbon separation, a topic that will be discussed in more detail in the context of classical molecular simulations of adsorption in MOFs (see section 3).

2.4.2. Periodic model studies

The adsorption of H_2 on MOF-505, a MOF based on a copper paddle-wheel unit like that of CuBTC but with 3,3'-5,5'-biphenyltetracarboxylate linkers (Figure 3), was studied by Yang *et al.* using a periodic PBE approach [73]. As expected, they found that the adsorption is preferential at the CUS with an energy of -13.4 kJ/mol for the H_2 molecule with its H-H axis normal to the Cu-Cu vector. The calculated energies for adsorption in locations between the oxygen atoms of two adjacent carboxylate linkers were ~-9 or ~-10 kJ/mol depending on the orientation of the H_2 molecule. Due to the small size of the adsorbate, these similarities in the interaction energies suggest that the most favourable adsorption configuration is only found at very low coverages and that clusters of H_2 molecules will be found for high uptakes. Kong *et al.* calculated a similar interaction energy, -12.5 kJ/mol, for the primary site on the Zn-MOF-74 (Figure 1) but using the vdW-DF approach [74]. The distance between the molecule and the Zn centre calculated by the vdW-DF approach, 2.9 Å, overestimated the experimental distance of 2.6 Å. Despite this problem, the vdW-DF approach successfully predicted four different binding sites for the H_2 molecule interacting with the Zn-MOF-74 in agreement with experimental 4K inelastic neutron scattering evidence [75]. In the isostructural Mg-MOF-74 material, Figure 1, the very recent study by Lopez *et al.* [40] employing also the vdW-DF approach predicts a binding energy of -14.5 kJ/mol, which is in reasonable

agreement with the experimental isosteric heat of adsorption (-10.1 kJ/mol) determined by Zhou *et al.* [11]. For the same material, i.e., Mg-MOF-74, the calculated interaction energies for H_2 were -24.8 kJ/mol and -6.0 kJ/mol with the LDA-PZ and GGA-PBE approaches, respectively [11]. The latter authors also performed calculations for other isostructural MOF-74 having Mn, Co and Ni metal centres, and found that despite the absence of dispersion interactions, both GGA and LDA were able to reproduce the trend of the experimental isosteric heats of adsorption, i.e., the binding energies followed the order Zn <Mn< Mg < Co < Ni. Zhou *et al.* [11] concluded that the major contribution between the CUS and the H_2 molecule is Coulomb attraction, and found a clear correlation between the empirical ion radius of the transition metals, the calculated M-H_2 distances, and the experimental isosteric heats of adsorption: the smaller the ion radius, the higher the interaction energy between the H_2 molecule and the MOF. Sillar *et al.* [36] considered the PBE-D2 approach to study the interaction between H_2 and MOF-5, an isoreticular MOF with oxide-centred Zn_4O tetrahedra and 1,4-benzenedicarboxylate linkers but without CUS. These authors found that the interaction energies originated from the consideration of either periodic or cluster models and the PBE-D2 approach were similar to the MP2 energies using triple and quadruple zeta basis sets with BSSE corrections. They concluded that dispersion is the major contribution for H_2 binding to MOF-5 and that the local environment around the binding sites determines the adsorption properties [36]. Interestingly, in two separate studies with MOFs presenting CUS, i.e., M-MOF-74 (M=Mg, Ni, Zn), Figure 1, dispersion forces between gaseous molecules and the surrounding MOF framework were also found to account for about one-half of the adsorption enthalpy [26,38].

In the case of CO_2, Grajciar *et al.* [53] reported a very complete study, combining experimental Tian-Calvet type microcalorimetry and quantum-mechanical

computations to investigate the interaction of this molecule with CuBTC. The calculations considered a periodic model representation of the MOF and a DFT-CC approach based on the PBE functional with corrections taken from CCSD(T)/CBS calculations for several different CO_2-molecular fragment systems optimised at the PBE/aug-cc-pVDZ level of theory. The calculated interaction energy at the CUS in the low coverage regime was -28.2 kJ/mol, which is in excellent agreement with the experimental result (-29 kJ/mol) reported by the same authors. In the optimal configuration, carbon dioxide is bridging the metal and the aromatic rings, with one of its oxygen atoms pointing towards a Cu atom and with the other oxygen pointing towards a hydrogen atom from the organic linker. As the number of CO_2 molecules in the system is increased, the interaction energy also increases to values between -29.1 and -31.5 kJ/mol, depending on the spatial arrangement adopted by the gaseous molecules, an energetic variation that follows the experimental trend [53]. A comparative study of CO_2 interaction performed for M-MOF-74 (Figure 1) and M-BTC (Figure 2), based on the original MOFs that demonstrated the highest CO_2 capacities at low pressure, with 18 different metals, i.e, the earth alkaline Be, Mg, Ca and Sr elements, the 3d elements from Sc to Zn plus Mo and W from group 6 and Sn and Pb from group 14, was reported very recently by Koh *et al.* [49]. These authors used the vdW-DF approach to calculate the interaction enthalpies (ΔH) at 300 K and found that the materials based on group 14 elements were the least interesting for CO_2 adsorption. Importantly, they identified 13 hypothetical compounds having enthalpies in the targeted thermodynamic window, i.e, $-40 \leq \Delta H \leq -75$ kJ/mol, namely M-MOF-74 with M=Mg, Ca, Sr, Sc, Ti, V, Mo and W, and M-BTC with M=Be, Mg, Ca, Sr and Sc, while all the other systems presented enthalpies less negative than the thermodynamic window [49]. Interestingly, as in ref. [64], these authors found that the partial charge at

the CUS correlated quite well with the ΔH values, which may be useful for screening purposes. Park *et al.* performed another comparative study for CO_2 adsorption on M-MOF-74 (PBE-D2 approach) [44]. They found that the experimental trend of the binding affinity, i.e., Mg > Ni > Co, was well reproduced by the PBE-D2 approach and suggested Ti and V metals to be the most promising for CO_2 capture [44]. Ti and V metals were among the most interesting ones in the case of M-DODBC but not in the case of M-BTC [49]. This is probably due to different coordination environments of the metal centres in the two structures. In fact, Poloni *et al.* [76] also performed DFT calculations including dispersion interactions, and suggested that not only the metal but also the organic linker is crucial in determining the CO_2 binding energetics in BTT-type MOFs (Figure 3) with Mg, Ca, Sr or Cu metals, due to the proximity between the linkers and the CUS. They showed that in this class of MOFs, the CO_2 binding is more sensitive to the organic linker than to the metal atom choice, i.e., organic linkers with atoms having large negative charges in the regions close to the CUS improve the electrostatic interactions with the CO_2 molecule. They found that replacing triazole with tetrazole (i.e., a CH is changed by N in the five-member ring) almost doubles the calculated interaction energy from -36 kJ/mol to -62 kJ/mol [76].

A very recent study appeared in the literature where periodic vdW-DF calculations were employed to unveil the molecular transport of H_2, CO_2 and H_2O in Mg-MOF-74 (Figure 1) [51] by finding the transition state structures with the climbing-image nudged elastic band method. Four key diffusion mechanisms were identified and confirmed by time-resolved in situ infrared spectroscopy data, i.e., two diffusion paths where a molecule hops from one Mg^{2+} site to another Mg^{2+} site in the same cell or in the next unit cell, and two other diffusion paths where a molecule moves through or around other molecules already in the material. The former two cases resemble situations at low

pressure, while the latter two correspond to situations with high degrees of saturation. The largest obstacles to flow were calculated for the water molecule (up to ~68 kJ/mol), while much smaller diffusion barriers were calculated for H_2 (up to ~15 kJ/mol). These barriers are similar to the corresponding calculated energies of interaction, in absolute value, with Mg-MOF-74. In the case of CO_2, a local minimum (secondary adsorption site) was also found and the barriers for diffusion are somewhat smaller than the calculated interaction energy, in absolute value.

3.Grand-canonical Monte Carlo simulations

3.1.Classical Molecular Simulations of Adsorption

As we have seen in the previous section, quantum-mechanical calculations are extremely useful to elucidate the underlying nature of adsorption in MOFs with CUS, and accurate adsorption energies and geometries can be obtained. However, such studies are inherently limited to small systems and cannot take into account the statistical distribution of adsorbate molecules at temperatures and pressures that are relevant to experiment. In order to achieve adsorption predictions that are directly comparable to experimental data, one must resort to classical methods based on statistical mechanics, such as molecular simulation. Classical molecular simulations of adsorption normally make use of the Grand Canonical Monte Carlo (GCMC) method [77] because it allows for the number of molecules to fluctuate at constant volume, temperature and chemical potential. The number of molecules in the simulation box (designed to represent the pore space of the adsorbent) equilibrates by particle exchanges with an infinite reservoir of adsorbate molecules [78]. By subsequently relating the chemical potential to the bulk-phase pressure, which is normally done by

applying an equation of state or by running separate simulations of the bulk phase, and converting the absolute adsorbed amount to excess adsorbed amount [79], one is able to obtain a simulated adsorption isotherm that can be directly compared to experimental data.

Naturally, the success of the GCMC method as a tool for predicting adsorption, and even for screening or designing porous materials, relies on the availability of a sufficiently accurate molecular model (also called "force-field") that can correctly describe the dominant intermolecular interactions in the system. The vast majority of adsorption simulation studies makes use of the Lennard-Jones (LJ) potential:

$$E_{\mathrm{LJ}} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{1}$$

The LJ potential is meant to represent repulsive interactions, arising from the overlap of atomic orbitals, and dispersion interactions, arising from mutually induced fluctuating (i.e., non-permanent) dipoles in two neighbouring molecules. The dependence of the dispersion energy with r^{-6} can be strictly derived from quantum mechanics [80], whereas the r^{-12} dependence of the repulsion energy is purely empirical in nature. The LJ potential is characterised by two parameters, the site diameter (σ) and the well depth (ε), where the subscripts i and j denote two individual sites. It is also common practice to include a term in the Hamiltonian to account for electrostatic interactions, normally assuming the form of Coulomb interactions between point charges:

$$E_{\mathrm{Coul}} = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \tag{2}$$

where q_i is the point charge on site i and ε_0 is the vacuum permittivity. By carefully calibrating the values of the point charges, it is possible to describe interactions between polar molecules (ionic, dipolar and even hydrogen bonds) with a reasonable degree of

accuracy. For non-polar molecules, such as alkanes, electrostatic interactions play a very small role and this term is usually neglected.

It is useful at this point to make a distinction between fluid-fluid and solid-fluid interactions. Generally speaking, the latter tend to dominate adsorption at low coverage, when adsorbate molecules are mostly interacting with the solid surface, while the former play an important role at high coverage, when the pore space is already largely occupied with adsorbed molecules. Selecting a model for fluid-fluid interactions is relatively straightforward, since several modern force-fields are able to describe pure-component bulk behaviour under a wide range of conditions (the TraPPE model [81], for example, is specifically designed to reproduce vapour-liquid equilibrium data). Modelling solid-fluid interactions, on the other hand, is much more challenging, mainly due to the difficulty in independently calibrating these parameters. In practice, most previous simulation studies of adsorption in MOFs simply apply parameters from general-purpose force-fields (e.g., UFF [82], DREIDING [83] or OPLS [84]) to model the solid framework atoms [85]. Combination rules, such as geometric averages or the Lorentz-Berthelot expressions [78], are then used to obtain cross-species solid-fluid parameters.

3.2. Predicting Adsorption in MOFs with CUS

3.2.1. Standard force-fields

Good agreement between experimental data and GCMC simulations using the standard, general-purpose, force-fields mentioned above has been reported in the past (see, for example, the pioneering work by Düren *et al.* [86]). However, recent studies demonstrate that these parameters tend to overestimate the strength of dispersion interactions, at least in some MOF materials. For example, Pérez-Pellitero *et al.* [87]

found that both UFF and DREIDING significantly overestimated adsorption of CH_4, CO_2 and N_2 in zeolitic imidazolate frameworks (ZIFs), where CUS are not present. To obtain good agreement with experiment, they rescaled the UFF interaction parameters by fitting them to reproduce methane adsorption in ZIF-8 at 303K. This modified force-field showed good transferability to other small gases adsorbed in materials of the same class. Similarly, Fairén-Jimenez *et al.* [88] observed an overestimation of dispersion interactions from UFF and DREIDING, and corrected them by scaling the UFF energy parameters by a factor of 0.77. This so-called UFF(+) model showed excellent agreement with experimental data for CO_2, CH_4 and larger alkanes in ZIF-8. Chen *et al.* [89] carried out an in-depth theoretical study of methane adsorption in CuBTC and clearly demonstrated that standard force-fields substantially overestimate dispersion interactions relative to accurate quantum-mechanical reference data. Finally, in another detailed theoretical study, McDaniel and Schmidt [90] analysed the physical origin of such discrepancies. They concluded that UFF overestimates the repulsion interaction at short distances and compensates this by overestimating the attractive dispersion interactions at large distances. As a consequence, UFF may yield good agreement for MOFs in which these two effects nearly cancel out, but leads to erroneous results when this is not the case.

If the performance of standard force-fields is problematic even in cases that are dominated by dispersion interactions, it becomes significantly worse for MOFs with CUS. As we have seen in the previous sections, both experimental and quantum-mechanical studies unequivocally demonstrate that a wide range of molecules interact specifically with unsaturated metals in MOFs, adsorbing at much shorter distances and with stronger energies than would be expected from dispersive interactions alone. This

is true for highly polar molecules such as water [52], but also, perhaps surprisingly, for non-polar molecules like methane [16, 22].

Several GCMC studies have shown that general-purpose force-fields that include only repulsion and dispersion components are unable to correctly represent the specific interactions between adsorbate molecules and the CUS. For example, Lamia *et al.* [91] carried out a combined simulation and experimental study of propane/propylene adsorption in CuBTC (Figure 2). While reasonable agreement was obtained for propane after applying a correction factor for the available pore volume of the real MOF material, propylene adsorption isotherms were severely underestimated by GCMC simulations based on the DREIDING model. The authors attributed this discrepancy to the specific interactions of the propylene double-bond with the unsaturated Cu atom, which were not correctly described in the simulations. These specific interactions were also responsible for a higher heat of adsorption for propylene and for a pronounced colour change in the CuBTC material, due to the change in the coordination environment of the Cu atom upon propylene adsorption. In two independent studies combining experiment and simulation, Getzschmann *et al.* [16] and Wu *et al.* [22] obtained congruent results when they compared the adsorption sites for methane in MOFs with unsaturated Cu atoms obtained from GCMC simulations and from neutron diffraction. While neutron diffraction showed that methane adsorbs significantly at the CUS, the GCMC simulations based on standard force-fields did not identify this adsorption site and showed adsorption only in regions dominated by strong dispersion interactions. Interestingly, while simulated adsorption isotherms in CuBTC at cryogenic temperatures were in significant disagreement with experimental measurements, they showed reasonable agreement at high temperatures and pressures (with a slight underestimation) [16]. In light of the mechanistic discrepancies described previously,

this agreement under conditions that are much less sensitive to the details of the molecular interactions is most likely due to error compensation (i.e., standard force-fields strongly underestimate adsorption at the CUS, but overestimate dispersion everywhere else). Other GCMC simulations for small alkanes and for small low-polarity gases like O_2 and N_2 were unable to detect significant adsorption at the unsaturated metal sites [92].

Similar observations have been made for molecules of intermediate polarity. In a systematic comparison between GCMC simulations using the UFF model and experimental data for hydrogen adsorption on different samples of CuBTC, Liu *et al.* [93] observed a severe underestimation of adsorption at low pressures, where the effect of solid-fluid interactions is largest. Importantly, in a subsequent study [94], the same group showed that the inclusion of electrostatic interactions in the model, by employing DFT-derived point charges, was not enough to account for this discrepancy. This strongly supports the argument that the differences are due to the inability of the UFF model to describe specific adsorption at the CUS. Fischer *et al.* [63, 95] reached similar conclusions in a comparative study of H_2 adsorption in several different MOFs, including four structures with unsaturated metal sites. Apart from underestimating adsorption isotherms in those materials, their GCMC simulations were unable to identify the CUS as preferential adsorption sites, in stark contrast to neutron diffraction experiments [95]. The authors went even further and established a correlation between the magnitude of the adsorption underestimation and the density of CUS in each MOF [63]. In their comparative study of CO_2 adsorption in a series of different MOFs, Yazaydin *et al.* [96] also observed significant discrepancies between experiment and GCMC simulations, particularly at low pressure and for MOFs with a high density of CUS. As in the case of hydrogen, these differences were not resolved by the inclusion

of electrostatic interactions in the model. Hamon *et al.* [97] also reported the inability of the DREIDING force-field in predicting adsorption of CO_2/CH_4 mixtures in MIL-100(Cr), and attributed the discrepancies to the existence of CUS in this MOF framework.

In what may appear as a paradox, standard force-fields actually seem to be more successful at describing adsorption of highly polar molecules in CUS-containing MOFs, at least in a qualitative sense. Indeed, significant adsorption at the metal sites was observed in studies that used the conventional LJ+charges approach to simulate adsorption of CO [98, 99, 100], water [101] and ammonia [102] on CuBTC, even though no adjustments were made to specifically account for adsorption at the CUS. This suggests that, in contrast to less polar molecules, purely electrostatic interactions play a much more significant role in these cases. It is important to notice, however, that the results were quite sensitive to small changes in the interaction parameters [99, 100, 101]. In particular for the case of water, the performance of the model depended dramatically on the choice of point charges, with some sets yielding rather unrealistic results [101]. Based on this limited number of studies, it is quite difficult to establish whether or not the conventional models are doing a good job at capturing the correct nature and magnitude of the specific fluid-CUS interactions for highly polar adsorbates, and error cancellation can by no means be ruled out at this stage.

3.2.2. Recalibrated force-fields

The above studies clearly establish that conventional models are inadequate for describing adsorption in CUS-containing MOFs (with the possible exception of highly polar adsorbates). A few authors have attempted to circumvent these limitations by applying the simplest possible approach – refitting some of the LJ parameters for the solid-fluid interactions. For instance, Yang and Zhong [73] identified the CUS as

preferred adsorption sites for hydrogen based on DFT calculations. They then performed GCMC simulations based on the OPLS-AA force-field [84], but refitted the LJ energy parameters for the framework oxygen and copper atoms in order to obtain better agreement with experimental adsorption isotherms. Reasonable agreement was indeed obtained, but with a systematic underestimation of adsorption at low pressure. More importantly, snapshots from GCMC simulations did not show evidence of H_2 adsorption at the CUS, in stark contrast with evidence coming from their own DFT calculations. In their study of propane/propylene separation, Lamia *et al.* [91] proposed a modified LJ energy parameter for the interaction of the copper atom with the sp^2 sites of propylene to account for the specific adsorption of olefins at the metal site, adjusting this parameter by fitting a single point on the isotherm at 323K. The aim was to show that describing the specific interaction with the CUS required energies that went well beyond the scale of purely dispersive interactions, and indeed they obtained energies consistent with coordination-type bonds. Moreover, perhaps fortuitously, good agreement was obtained between GCMC simulations and experimental isotherms at several other temperatures. In a more detailed later study, however, Jorge *et al.* [103] showed that the modified LJ model did not lead to specific adsorption of olefins at the CUS, and thus to a realistic adsorption mechanism.

These previous studies clearly demonstrate that simple adjustments to standard force-field parameters are not likely to yield an accurate representation of the underlying mechanism of adsorption in MOFs with CUS, and that more sophisticated approaches are necessary. In Figure 5, we compare potential energy maps and adsorption isotherms for propylene adsorption in CuBTC, obtained from the standard DREIDING force-field, the modified model of Lamia *et al.* [91] and a more accurate approach involving a combination of QM and GCMC (described in detail in section

3.2.3). First of all, it is clear that the DREIDING model is unable to capture the specific interactions at the CUS (Figure 5a), leading to a massive underestimation of propylene adsorption (Figure 5d). The second observation that can be made is that a simple "ad-hoc" modification of the LJ energy parameter is also not able to capture the strong interaction at the CUS, instead enhancing the interaction energy elsewhere in the pore space (Figure 5b). This also highlights the fact that obtaining good agreement between simulated and experimental adsorption isotherms (Figure 5e) is not sufficient to be certain that the model is realistic. In this case, a realistic description of *both* the adsorption isotherms and the adsorption mechanism could only be obtained by a more sophisticated approach whereby QM-calculated adsorption energies are incorporated into the classical simulation model (Figures 5c and 5f). In the following section, we provide an overview of these new modelling approaches.

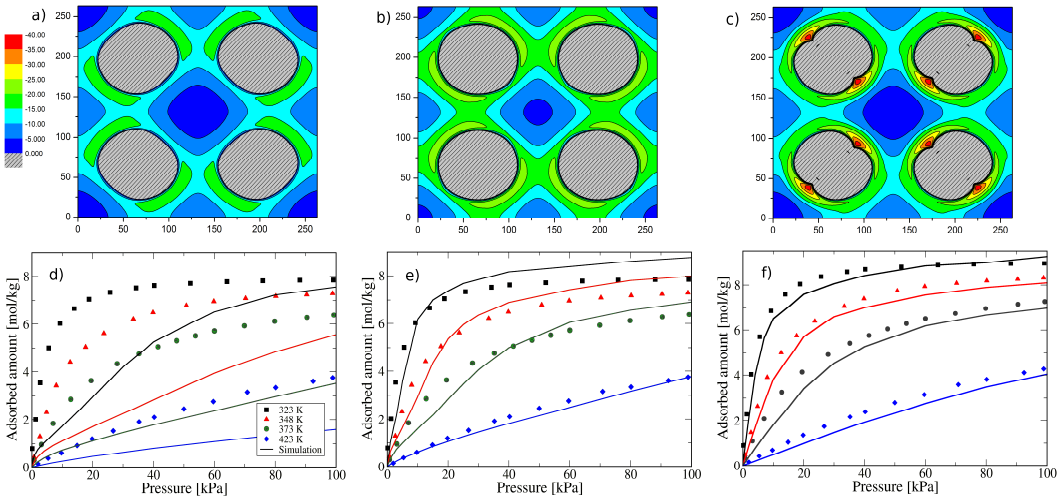

Figure 5. *Simulated potential energy maps (top row) and adsorption isotherms (bottom row) for propylene on CuBTC using different force-fields. The maps are for the [100] plane of CuBTC, intersecting the paddle-wheel units along the Cu-Cu axes, which are oriented along the two main diagonals of the box. Red represents the strongest attractive interactions (energy scale shown on the left-hand side), while the grey areas*

are dominated by repulsive interactions and hence inaccessible to adsorbate molecules. The simulated isotherms (lines) are compared to experimental data (points) at 4 different temperatures. Plots a) and d) were obtained using the standard DREIDING model, plots b) and e) were obtained with the modified DREIDING model, as proposed by Lamia et al. [91], while plots c) and f) correspond to the combined QM+GCMC method [104].

3.2.3. Hybrid QM+GCMC approaches

Recent attempts to achieve a more realistic description of adsorption in MOFs with CUS have relied on a combination of QM and classical simulation methods, and three strategies can be distinguished: 1) Complete parameter refitting based on QM energies (often using functional forms that depart from the standard LJ potential); 2) Incorporation of QM-based interactions between adsorbates and CUS into standard LJ-based force-fields; 3) Direct use of QM-based energy grids for the solid-fluid interactions, thus avoiding the use of empirical functions and parameters altogether. In what follows, these will be considered in turn.

Ab initio-derived force-fields have been around for decades, but have mainly been restricted to modelling fluid-fluid interactions (see, e.g., [105] and references therein). In recent years, however, several studies have attempted to parameterise solid-fluid interactions from first principles, with the aim of modelling adsorption in porous materials [106]. The process involves essentially three steps: i) calculation of adsorption energies of a given adsorbate in the material of interest; ii) fitting of these energies to an appropriate functional form; iii) GCMC simulations of adsorption using the QM-derived functions and parameters. The first step can be carried out on periodic models of the framework or on smaller cluster models – the former are more realistic but more

computationally demanding, and thus normally restricted to lower-level methods – at different levels of theory – from Hartree-Fock, to DFT, to coupled-cluster – and with different degrees of geometrical optimisation – ranging from single-point calculations at the crystallographic positions to full geometry optimisations of the adsorbed complexes (see Section 2 for a more detailed description of QM calculations). Similarly, the functions used in the second step can vary widely in complexity, with simpler functions like the LJ potential being more easily incorporated into standard simulation packages at the cost of reduced accuracy in matching the QM energy profiles.

QM-based force-fields have been derived for zeolites [107], covalent organic frameworks, or COFs [108, 109, 110], microporous organic crystals [111], and MOFs without unsaturated metal sites [90, 112, 113, 114, 115]. These systems, however, are dominated by dispersion interactions (with electrostatics sometimes also playing an important role), and are thus not directly relevant to this review. Perhaps more relevant are studies that attempt to model interactions between adsorbates and metal-doped or metal-functionalised MOFs and COFs, the modelling of which has been described in several recent reviews [106, 116, 117, 118]. In these systems, the metal cations are much more exposed than in the case of CUS, and hence purely electrostatic interactions are dominant. In this review, we focus only on studies that deal specifically with capturing interactions between adsorbate molecules and CUS in MOFs, and direct the interested reader to the above publications, and references therein.

We are aware of only two studies proposing fully *ab initio* force-fields for MOFs that possess CUS [119, 120]. Chen *et al.* [119] developed a QM-based force-field for adsorption of CO_2 in Mg-MOF-74 and CH_4 in CuBTC using two sets of adsorption energy data as reference for the parameterisation. For CO_2, they used adsorption energies for several different orientations of the adsorbate around a cluster

model of the MOF, calculated by DFT using B2PLYP (a double-hybrid functional) [121] with an empirical dispersion correction [46]. For CH_4, they used previously calculated adsorption energies on a periodic model of CuBTC using the DFT/CC method [122], which introduces a correction term to account for the differences between DFT and a high-level coupled-cluster approach. To fit the DFT energies, they used a three-parameter modified Buckingham potential for all solid-fluid interactions except those involving the CUS, together with a complex piece-wise expression with five parameters, involving a Morse potential, an r^{-6} term and a cubic spline, for the interactions between the adsorbates and the CUS. The authors went to a great length to justify their choice of functional form, showing that simpler functions such as the Morse and LJ models were unable to accurately fit the QM adsorption energies in the entire range of distances. In particular, the authors emphasised the need to correctly capture the anisotropy of the potential energy surface around the CUS without artificially enhancing the interaction energy away from those sites. GCMC isotherms calculated using their force-field were in very good agreement with experimental data, and the transferability of the model for methane was demonstrated by predicting adsorption isotherms on a different MOF, PCN-14, containing a similar type of CUS.

In a recent paper, Dzubak *et al.* [120] developed an *ab initio* force-field for adsorption of CO_2 and N_2 in Mg-MOF-74 (Figure 1), which contains unsaturated metal sites, by applying the NEMO methodology [105] to decompose the QM adsorption energy. Energies were calculated at the MP2 level for different paths where the gas molecules approached small cluster models cut out from the MOF framework. After performing a NEMO energy decomposition, several components of the energy were grouped together such that the final force-field expression comprised a Buckingham potential for the repulsive term, a Coulomb term for the electrostatic (first moment)

contributions, and an attractive part composed of a sum of r^{-6} and r^{-5} terms. Isosteric heats of adsorption and isotherms calculated using the new force-field yielded good agreement with experimental data, in a marked improvement over predictions based on the UFF model (which, as we have discussed, does not adequately consider interactions with the CUS). Nevertheless, the authors observed a slight overestimation of experimental adsorption, and interpreted this as a consequence of not all the CUS sites of the MOF being accessible to the adsorbate molecules. Transferability of the model was demonstrated by successfully predicting adsorption of CO_2 in Mg_2(dobpdc), which contains the same atom types as Mg-MOF-74 and has a very similar structure, and in MOF-5, which does not contain CUS, and for which new parameters had to be determined by the same combined QM+GCMC approach. As recognised by the authors, the success of their approach hinged on a correct account of the interactions close to the CUS, namely on a correct balance between the attractive electrostatic and orbital interactions and the repulsive term. Interestingly, when Dzubak *et al.* extended their approach to Zn-MOF-74 (i.e., simply replacing Mg by Zn in the original material), it was only necessary to derive new parameters for interactions with Zn, while all other interactions remained virtually unaffected. This strongly suggests that parameters for adsorbate-CUS interactions can be determined independently from other types of interactions, which is a particularly relevant conclusion for the approach described below.

Solid-fluid force-fields derived entirely from QM calculations have the potential advantage of high accuracy, but are more difficult to transfer to other systems – different adsorbates and/or adsorbents than those used to parameterise the model. For instance, in the work of Dzubak *et al.* [120], significantly different parameters were used for the interactions between CO_2 and aromatic carbon atoms in Mg-MOF-74 and

in MOF-5, even though those framework atoms are chemically very similar. An alternative approach that aims to improve transferability, perhaps at the cost of some accuracy, is to incorporate additional terms into a pre-existing solid-fluid molecular model (usually of the LJ form) to account only for the specific interactions with the CUS. This approach was pioneered by Fischer and co-workers [61, 123, 124] and also applied by Gomez *et al.* [125]. We will begin by describing the general approach, using our most recent work [61] as a basis, and then discuss the differences between previous approaches in more detail.

Our approach involves several sequential steps, depicted schematically in Figure 6. The first step is to carry out quantum-mechanical calculations of the adsorption energy for the molecules of interest at the CUS, where the distance between the adsorbate and the metal is varied in small increments so as to obtain a potential energy profile. Again, this may involve either periodic or cluster calculations (see section 2). In a detailed study of ethylene adsorption on several cluster models of CuBTC [61], we have shown that although the cluster that most resembled the framework structure (i.e., $Cu_2(btc)_4$) performed best, the effect of cluster size was not very significant, and reasonable energies could be obtained using relatively small clusters such as $Cu_2(formate)_4$. We also analysed the effect of the degree of optimisation (ranging from single-point calculations on fixed geometries to full optimisation at each step), and observed that inclusion of flexibility of the Cu-Cu axis of the MOF and of the C=C bond of the adsorbate led to better results. However, the overall effect on adsorption energies and on the final simulated isotherms was relatively small. Another important variable is the level of theory of the QM calculations, with most studies relying on DFT. As discussed in section 2, issues like the basis set size, the choice of exchange-correlation functional, and the consideration, or not, of dispersion corrections, are likely

to have a strong effect on the performance of the multiscale hybrid models. More systematic studies on the effect of these variables are needed, and we are currently pursuing this avenue of research [126].

In principle, the QM energies are the result of several different contributions (see, e.g., [105]), some of which are already, implicitly or explicitly, included in the standard LJ force-field. An obvious example of this is repulsion, which is responsible for the steep increase in the QM energy profiles at short distances, but already forms an intrinsic part of all LJ solid-fluid models. As such, the next step of our procedure is to decompose the QM energy into its different components, extracting only the contribution due to the specific interaction with the CUS. This is by no means a trivial procedure, and often requires several assumptions, the nature of which will be discussed in more detail below. Once the fluid-CUS energy profile is computed, it can be fit to an appropriate functional form and the corresponding parameters extracted. The next step is to incorporate these specific interaction energies into the GCMC simulation, which may or may not involve the creation of new interaction sites in the model of the adsorbate molecule. Finally, the realism and predictive ability of the model can be assessed by calculating potential energy maps, preferential adsorption sites, adsorption isotherms, isosteric heats of adsorption, etc. Several of these properties can be directly or indirectly compared to experimental data, thus providing adequate validation for the model and helping to identify possible routes for improvement.

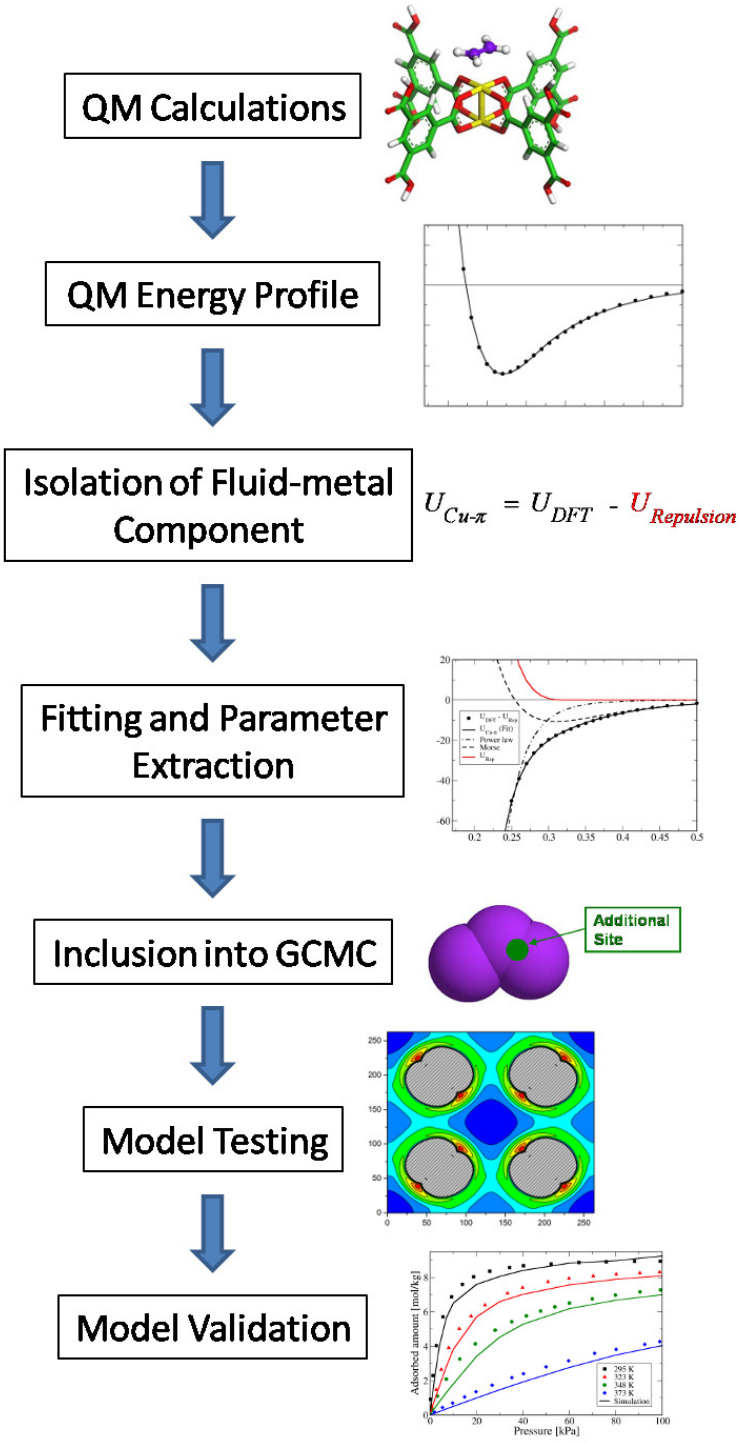

Figure 6. *Diagram showing the general approach for developing hybrid QM+GCMC models to predict adsorption in MOFs with unsaturated metal sites. QM calculations are first carried out to obtain an adsorption energy profile for the adsorbate interacting with the CUS. The specific contribution of the fluid-metal interaction is then extracted from the QM energies and fit to an appropriate functional form. The fluid-metal*

interaction is then incorporated into the molecular model, and adsorption is predicted by GCMC simulations. The pictures on the right-hand side are illustrations of each step of the procedure, based on our simulations of propylene adsorption on CuBTC [61].

Although the approach depicted in Figure 6 is quite general, its practical implementation for different systems may vary substantially, and different assumptions may be involved at specific stages of the process. In their study of hydrogen adsorption in MOFs, Fischer *et al.* [123] obtained their QM adsorption profiles from DFT single-point calculations on a pre-optimised $Cu_2(bc)_4$ cluster (see Figure 2) using the PBE functional and a double-numerical plus polarisation (DNP) basis set. Because the PBE functional is not able to properly account for long-range dispersion interactions, the authors assumed that their DFT-derived energies directly corresponded to the H_2-CUS specific interaction (i.e., they omitted the third step in Figure 6). They then fitted the DFT profile to a Morse function, since this provided a much more satisfactory description of the adsorption energy profile than the LJ functional form. The Morse potential was then straightforward to incorporate into their united-atom model of hydrogen, as a specific interaction between the single H_2 site and the Cu atom of the MOF. Purely electrostatic interactions were neglected entirely, since they had previously been shown to have only a small effect on the adsorption isotherms for these systems [95]. Finally, the authors also considered the effect of different orientations of the H_2 molecule (possible in reality, but absent in the united-atom model) by applying a scaling factor of 2/3 to the interaction energy. This orientationally averaged model yielded isotherms for hydrogen adsorption in CuBTC and PCN-12 (two MOFs based on the Cu paddle-wheel motif) that were in excellent agreement with experiment. Furthermore, their model also showed a remarkable improvement over standard LJ

force-fields for H_2 adsorption in the $(Cu_4Cl)_3(btt)_8$ MOF, which also contains unsaturated Cu sites, but in a different inorganic building unit. However, agreement in this case was not as good as for the original paddle-wheel-based MOFs, suggesting that a separate parameterisation of adsorption on the Cu site of $(Cu_4Cl)_3(btt)_8$ would improve the quality of the predictions. The model of Fischer *et al.* was used in a later study by Düren and co-workers [127] to successfully predict thermal desorption spectra of H_2 on CuBTC.

Sastre and co-workers [125] also developed a hybrid model for hydrogen adsorption in MOFs with the Cu-paddle-wheel using a procedure that was similar to the one depicted in Figure 6. They calculated the optimised adsorption energy for H_2 on a $Cu_2(bc)_4$ cluster by DFT with the SSB-D functional (meant to account for dispersion interactions), and the def2-TZVP basis set. However, instead of fitting their model to a full adsorption energy profile, they estimated parameters for both a LJ and a Morse potential based solely on the energy and H_2-Cu distance at the minimum. The authors also showed that, at least for this system, purely electrostatic interactions played only a marginal role and could be implicitly included in other components of the model. They validated their model by comparing average H_2 occupancy maps on CuBTC, computed using molecular dynamics (MD), to experimental neutron diffraction data. Interestingly, they confirmed the conclusion of Fischer *et al.* that only the Morse potential, and not the LJ, was able to provide an accurate description of the interaction energy near the metal site. Adsorption probability distributions from their model yielded good qualitative agreement with experiments for several different MOFs containing CUS. However, adsorption isotherms for H_2 in CuBTC (given in their Supporting Information) significantly overestimated experimental data. A possible reason from this discrepancy is that their model was effectively double-counting dispersion interactions. Since their

DFT functional included a correction to account for dispersion, the DFT adsorption energy contained contributions arising from dispersion interactions between H_2 and the framework (including with atoms other than Cu). However, in their fitting procedure, Gomez *et al.* did not account for this fact (they essentially skipped the third step in Figure 6), with the end result that their specific H_2-Cu potential included dispersion contributions that were already included in the DREIDING force-field. Because Fischer *et al.* used a DFT functional (PBE) that was not meant to capture dispersion interactions in the first place, their assumption of zero contribution of dispersion to the DFT energy was much more reasonable, and led to better quantitative predictions of adsorption [123].

Fischer *et al.* [124] also parameterised a model for adsorption of CO_2 and acetylene on CuBTC. As reference QM energies, they once again used DFT-PBE profiles, but this time on a smaller $Cu_2(formate)_4$ cluster. They fitted the DFT profiles to the LJ functional form, but attempted to mitigate the possible double-counting of interactions by explicitly taking into account electrostatic interactions between the adsorbate and the Cu-formate cluster (using QM-determined point charges), as well as LJ interactions between the adsorbate and the two oxygen atoms closest to the CUS in their fitting procedure. As before, the hybrid model showed a remarkable improvement over the standard UFF model, yielding reasonable agreement with experimental isotherms for both gases. Nevertheless, a slight underestimation of adsorption could still be observed, particularly for acetylene at low pressures and for carbon dioxide in the entire pressure range, which is probably related to the assumptions described above.

In a recent paper [61], we carried out a detailed analysis of methodological aspects related to the hybrid QM-GCMC approach, applying it to model the adsorption of propane and propylene on CuBTC. After finding the best cluster size and degree of

optimisation for the DFT cluster calculations with the PBE functional, we isolated the contribution due to the specific interaction of the C=C double bond with the CUS by assuming that the dispersion component of the DFT energy was zero and subtracting the contribution due to repulsive interactions (already included in the DREIDING force-field) from the original DFT profile. For this purpose, we applied the Weeks-Chandler-Andersen approach [128], together with a Monte Carlo procedure to compute the minimum repulsive energy at each value of the distance between the centre of the C=C double bond and the Cu atom. The resulting purely attractive curve was fit to an expression combining a Morse function and a power law term to represent the asymptotic limit at short distances. An extra site was added to the propylene model at the centre of the double bond, and this site interacted only with the Cu atom by way of the fitted potential energy. Predictions of propylene adsorption isotherms were in excellent agreement with experimental data, while binary propane/propylene isotherms were significantly different from predictions using ideal adsorbed solution theory (IAST) [129]. We have recently implemented some technical improvements to our method, including the use of a more realistic cutoff scheme, and extended it to describe ethane/ethylene adsorption on the same MOF [104]. As we can see from Figure 5c, this approach is now able to realistically describe the potential energy surface in CuBTC, as well as accurately predict adsorption isotherms of olefins on this MOF (Figure 5f), showing a massive improvement over the standard DREIDING model.

The last approach we consider in this section completely bypasses the need for empirical functions and parameters. Instead, it makes direct use of QM-based potential energy grids, calculated on a periodic model of the framework. To our knowledge, the only paper to adopt such an approach is that of Chen *et al.*, who applied it to model the adsorption of methane on CuBTC [89]. They constructed an interaction energy grid

from periodic QM calculations with the DFT/CC method [122], which includes a pairwise correction term to account for the differences between standard DFT energies and highly accurate CCSD(T)/CBS reference values. The solid-fluid interaction was calculated on-the-fly from this grid during the GCMC simulations, instead of relying on a specific functional form. The location of the main adsorption sites computed from their model was in very good agreement with experimental neutron diffraction data [16], as were methane adsorption isotherms at cryogenic temperatures. Simulations of adsorption at high temperatures, however, somewhat underestimated adsorption except at the very high pressure range. Importantly, the authors analysed the impact of the choice of DFT approach on the adsorption isotherms, and concluded that not even dispersion-corrected functionals were able to provide a correct description of the adsorption energies in this system. Although the approach of Chen *et al.* is undoubtedly the most accurate method to include adsorbate-metal interactions in classical GCMC simulations, it involves rather computationally demanding QM calculations (both for the calibration of the DFT/CC method and for generating the periodic potential energy grid). More importantly, it is hard to see how it might be applicable to non-spherically symmetric adsorbates, for which it would be necessary to take into account different molecular orientations at each grid point.

4. Conclusions

There is mounting evidence, coming from both theory and experiment, showing that a wide range of adsorbate molecules interact specifically with coordinatively unsaturated metal sites present in some MOF materials. These interactions are highly localised, most often involving electron donation between orbitals of the adsorbate and of the metal, and can significantly change the behaviour of the material relative to what would be expected based on van der Waals and electrostatic interactions alone. The nature of

these interactions poses a significant challenge for molecular simulation, and requires the use of sophisticated multiscale modelling approaches.

Quantum-mechanical methods are extremely useful tools to obtain fundamental insight into the nature of adsorbate-CUS interactions, and can potentially yield accurate values for adsorption energies and geometries. Among other things, recent studies have shown that changing the metal site in a MOF can have a profound effect on the adsorption energy, with differences of nearly an order of magnitude sometimes being observed. Moreover, changing or functionalising the organic linker in some MOFs can also significantly affect the adsorption energy at the CUS, due to steric or electronic effects (or both). Some of these effects, however, have not yet been demonstrated experimentally, and QM results must therefore be interpreted with caution, since they not always adequately account for all the variables present in experiments. Indeed, application of QM methods to MOFs is still challenging, and a balance must be struck between computational accuracy (i.e., level of theory) and realism of the model (i.e., periodic vs. cluster approaches, and cluster size effects). Further research is clearly necessary to find an "optimal" QM strategy to study adsorption in MOFs with CUS.

The situation is perhaps even more challenging for classical simulations, since it is now clear that conventional "off-the-shelf" force-fields based on Lennard-Jones plus electrostatics are not able to accurately describe adsorption at the CUS. Ad-hoc tuning of selected potential parameters to match experimental data is not recommended, as it will almost certainly lead to incorrect adsorption mechanisms. In fact, this approach can often yield good agreement with experimental data based on fortuitous error cancellation – further evidence of the fact that getting the isotherms right does not necessarily mean that the model is correct. In recent years, more sophisticated approaches, combining QM with GCMC, have appeared, generally leading to dramatic

improvements in adsorption predictions relative to conventional models. These hybrid approaches come in different flavours, each with advantages and shortcomings. Constructing QM energy grids for direct use in GCMC simulations, without the need for parameter fitting, is potentially the most accurate approach, but is rather limited in transferability (a new grid would have to be generated for each MOF, and this is often an expensive procedure) and in general applicability (it is so far limited to spherically symmetric adsorbates). Complete fitting of force-field parameters based on QM reference energies can also lead to highly accurate predictions, but transferability is still an unresolved issue, as sometimes rather different parameters are attributed to chemically similar atoms in different MOFs. We have followed a different approach, the idea of which is to incorporate a QM-based term into an otherwise conventional LJ-based model. This significantly improves transferability and ease of application at the cost of some accuracy. The added advantage of our method is that specific interactions with CUS are treated separately from dispersion and electrostatic interactions, and it will therefore benefit directly from improvements in conventional models as they become available. Furthermore, the method can also be improved by lifting some of the assumptions associated with the energy decomposition and by using more accurate QM approaches to obtain reference energies. So far, we have applied our approach only to a restricted number of systems, but research is underway to extend it to a wide range of adsorbates and MOFs containing coordinatively unsaturated metal sites.

Acknowledgments

M. Fi. gratefully acknowledges a postdoctoral fellowship by the German Research Foundation (DFG grant Fi 1800/1-1). J. R. B. G. holds an *Investigador FCT* position, financed by Fundação para a Ciência e a Tecnologia, Portugal.

References

[1] Férey, G. *Hybrid porous solids: past, present, future.*Chem. Soc. Rev.37 (2008), pp. 191–214.

[2] Chemical Society Reviews themed issue: *Metal-organic frameworks*, 8 (2009), pp. 1201 ff.

[3*] Chemical Reviews* thematic issue: *Metal-organic frameworks*, 112 (2012), pp. 673 ff.

[4] M. Dincă and J. R. Long, *Hydrogen storage in microporous metal-organic frameworks with exposed metal sites,*Angew. Chem., Int. Ed. 47 (2008), pp. 6766–6779.

[5] E. D. Bloch, W. L. Queen, R. Krishna, J. M. Zadrozny,C. M. Brown, and J. R. Long, *Hydrocarbon Separations in a Metal-Organic Framework with Open Iron(II) Coordination Sites,*Science 335 (2012), pp. 1606–1610.

[6] L. Alaerts, E. Séguin, H. Poelman, F. Thibault-Starzyk, P. A. Jacobs, and D. E. De Vos, *Probing the Lewis acidity and catalytic activity of the metal-organic framework* $[Cu_3(btc)_2]$ *(BTC=benzene-1,3,5-tricarboxylate).*Chem. Eur. J. 12 (2006), pp. 7353–7363.

[7] H. Li, C. E. Davis, T. L. Groy, D. G. Kelley, and O. M. Yaghi, *Coordinatively Unsaturated Metal Centers in the Extended Porous Framework of* $Zn_3(BDC)_3{\cdot}6CH_3OH$ *(BDC = 1,4-Benzenedicarboxylate).*J. Am. Chem. Soc. 120 (1998), pp. 2186–2187.

[8] S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, and I. D. Williams, *A Chemically Functionalizable Nanoporous Material* $[Cu_3(TMA)_2(H_2O)_3]_n$. Science 283 (1999), pp. 1148–1150.

[9] C. R. Wade, and M. Dincă, *Investigation of the synthesis, activation, and isosteric heats of* CO_2 *adsorption of the isostructural series of metal-organic frameworks* $M_3(BTC)_2$ *(M = Cr, Fe, Ni, Cu, Mo, Ru).*Dalton Trans. 41 (2012), pp. 7931–7938.

[10]N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, and O. M. Yaghi, *Rod packings and metal-organic frameworks constructed from rod-shaped secondary building units.*J. Am. Chem. Soc. 127 (2005), pp. 1504–1518.

[11] W. Zhou, H. Wu, and T. Yildirim, *Enhanced* H_2 *adsorption in isostructural metal-organic frameworks with open metal sites: strong dependence of the binding strength on metal ions.* J. Am. Chem. Soc. 130 (2008), pp. 15268–15269.

[12]H. Wu, W. Zhou, and T. Yildirim, *High-capacity methane storage in metal-organic frameworks* $M_2(dhtp)$*: The important role of open metal sites.*J. Am. Chem. Soc. 131 (2009), pp. 4995–5000.

[13] S. R. Caskey, A. G. Wong-Foy, and A. J. Matzger, *Dramatic tuning of carbon dioxide uptake via metal substitution in a coordination polymer with cylindrical pores.*J. Am. Chem. Soc. 130 (2008), pp. 10870–10871.

[14]H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gandara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O'Keeffe, O. Terasaki, J. F. Stoddart, and O. M. Yaghi, *Large-Pore Apertures in a Series of Metal-Organic Frameworks.*Science 336 (2012), pp. 1018–1023.

[15] V. K. Peterson, Y. Liu, C. M. Brown, and C. J. Kepert, *Neutron powder diffraction study of D_2 sorption in Cu_3(1,3,5-benzenetricarboxylate)$_2$.* J. Am. Chem. Soc. 128 (2006), pp. 15578–15579.

[16] J. Getzschmann, I. Senkovska, D. Wallacher, M. Tovar, D. Fairen-Jimenez, T. Düren, J. M. Van Baten, R. Krishna, and S. Kaskel, *Methane storage mechanism in the metal-organic framework $Cu_3(btc)_2$: An in situ neutron diffraction study.*Microporous Mesoporous Mater. 136 (2010), pp. 50–58.

[17] S. Xiang, W. Zhou, J. M. Gallegos, Y. Liu, and B. Chen, *Exceptionally high acetylene uptake in a microporous metal-organic framework with open metal sites.*J. Am. Chem. Soc. 131 (2009), pp. 12415–12419.

[18] H. Wu, J. M. Simmons, G. Srinivas, W. Zhou, and T. Yildirim, *Adsorption Sites and Binding Nature of CO_2 in Prototypical Metal−Organic Frameworks: A Combined Neutron Diffraction and First-Principles Study.* J. Phys. Chem. Lett. 1 (2010), pp. 1946–1951.

[19] S. Xiang, W. Zhou, Z. Zhang, M. A. Green, Y. Liu, Y., and B. Chen, *Open metal sites within isostructural metal-organic frameworks for differential recognition of acetylene and extraordinarily high acetylene storage capacity at room temperature.* Angew. Chem., Int. Ed. 49 (2010), pp. 4615–4618.

[20] M. Dincă, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann, and J. R. Long, *Hydrogen storage in a microporous metal-organic framework with exposed Mn^{2+} coordination sites.* J. Am. Chem. Soc. 128 (2006), pp. 16876–16883.

[21] M. Dincă, W. S. Han, Y. Liu, A. Dailly, C. M. Brown, and J. R. Long, *Observation of Cu2+-H2 interactions in a fully desolvated sodalite-type metal-organic framework.* Angew. Chem., Int. Ed. 46 (2007), pp. 1419–1422.

[22] H. Wu, J. M. Simmons, Y. Liu, C. M. Brown, X.-S. Wang, S. Ma, V. K. Peterson, P. D. Southon, C. J. Kepert, H.-C. Zhou, T. Yildirim, and W. Zhou, *Metal-Organic Frameworks with Exceptionally High Methane Uptake: Where and How is Methane Stored?*Chem. Eur. J. 16 (2010), pp. 5205–5214.

[23] C. Prestipino, L. Regli, J. G. Vitillo, A. Damin, F. Bonino, A. Zecchina, C. Lamberti, P. L. Solari, K. O. Kongshaug, and S. Bordiga, *Local Structure of Framework Cu(II) in HKUST-1 Metallorganic Framework: Spectroscopic Characterization upon Activation and Interaction with Adsorbates.*Chem. Mater. 18 (2006), pp. 1337–1346.

[24]S. A. Fitzgerald, B. Burkholder, M. Friedman, J. B. Hopkins, C. J. Pierce, J. M. Schloss, B. Thompson, and J. L. C. Rowsell, *Metal-Specific Interactions of H_2 Adsorbed within Isostructural Metal-Organic Frameworks.*J. Am. Chem. Soc. 133 (2011), pp.20310–20318.

[25] C. Volkringer, H. Leclerc, J. Lavalley, T. Loiseau, G. Férey, M. Daturi, and A. Vimont, *A. Infrared Spectroscopy Investigation of the Acid Sites in the Metal–Organic Framework Aluminum Trimesate MIL-100(Al).*J. Phys. Chem. C. 116 (2012), pp. 5710–5719.

[26]L. Valenzano, B. Civalleri, S. Chavan, G. Tunes Palomino, C. Otero Areán, and S. Bordiga, *Computational and Experimental Studies on the Adsorption of CO, N_2 , and CO_2 on Mg-MOF-74.*J. Phys. Chem. C. 114 (2010), pp. 11185–11191.

[27] M. Haouas, C. Volkringer, T. Loiseau, G. Férey, and F. Taulelle, *Monitoring the Activation Process of the Giant Pore MIL-100(Al) by Solid State NMR*.J. Phys. Chem. C. 115 (2011), pp. 17934–17944.

[28] X. Kong, E. Scott, W. Ding, J. A. Mason, J. R. Long, and J. A. Reimer, *CO_2 Dynamics in a Metal-Organic Framework with Open Metal Sites*.J. Am. Chem. Soc. 134 (2012), pp. 14341–14344.

[29] L.-C. Lin, J. Kim, X. Kong, E. Scott, T. M. McDonald, J. R. Long, J. A. Reimer, and B. Smit,*Understanding CO_2 Dynamics in Metal-Organic Frameworks with Open Metal Sites*. Angew. Chem., Int. Ed. 52 (2013), pp. 4410–4413.

[30]R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco, and M. Llunell, *CRYSTAL09 User's Manual*. University of Torino, Torino, 2009.

[31] K. Yu, K. Kiesling, and J. R. Schmidt, *Trace Flue Gas Contaminants Poison Coordinatively Unsaturated Metal−Organic Frameworks: Implications for CO_2 Adsorption and Separation*. J. Phys. Chem. C 116 (2012), pp. 20480−20488.

[32] R. A. Kendall, T. H. Dunning Jr., and R. J. Harrison, *Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions*. J. Chem. Phys., 96 (1992) pp. 6796-806.

[33] T. H. Dunning Jr., *Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen*. J. Chem. Phys. 90 (1989) pp. 1007-1023.

[34] J. H. Bak, V. –D. Le, J. Kang, S. –H. Wei, and Y. –H. Kim, *First-Principles Study of Electronic Structure and Hydrogen Adsorption of 3d Transition Metal Exposed Paddle Wheel Frameworks*. J. Phys. Chem. C 116 (2012) pp. 7386−7392.

[35] Y. Y. Sun, Y. –H. Kim, and S. B. Zhang, *Effect of Spin State on the Dihydrogen Binding Strength to Transition Metal Centers in Metal-Organic Frameworks*. J. Am. Chem. Soc. 129 (2007) pp. 12606-12607.

[36] K. Sillar, A. Hofmann, and J. Sauer, *Ab Initio Study of Hydrogen Adsorption in MOF-5*. J. Am. Chem. Soc. 131 (2009) pp. 4143–4150.

[37] K. Sillar, and J. Sauer, *Ab Initio Prediction of Adsorption Isotherms for Small Molecules in Metal−Organic Frameworks: The Effect of Lateral Interactions for Methane/CPO-27-Mg*. J. Am. Chem. Soc. 134 (2012) pp. 18354−18365.

[38] L. Valenzano, B. Civalleri, K. Sillar, and J. Sauer, *Heats of Adsorption of CO and CO_2 in Metal-Organic Frameworks:Quantum Mechanical Study of CPO-27-M (M = Mg, Ni, Zn)*. J. Phys. Chem. C 115 (2011) pp. 21777–21784.

[39] J. P. Prates-Ramalho, J. R. B. Gomes, and F. Illas, *Accounting for Van der Waals Interactions Between Adsorbates and Surfaces in Density Functional Theory Based Calculations: Selected Examples*. RSC Adv. in press.

[40] M. G. Lopez, P. Canepa, and T. Thonhauser, *NMR study of small molecule adsorption in MOF-74-Mg*. J. Chem. Phys. 138 (2013) pp. 154704-1:7.

[41] J. P. Perdew, and A. Zunger, *Self-interaction correction to density-functional approximations for many-electron systems.* Phys. Rev. B 23 (1981) 5048-5079.

[42] J. P. Perdew, K. Burke, and M. Ernzerhof, *Generalized gradient approximation made simple.* Phys. Rev. Lett. 77 (1996) 3865-3868.

[43] J. P. Perdew, K. Burke, and M. Ernzerhof, *Erratum: Generalized gradient approximation made simple.* Phys. Rev. Lett. 78 (1997) 1396-1396.

[44] J. Park, H. Kim, S. S. Han, and Y. Jung, *Tuning Metal−Organic Frameworks with Open-Metal Sites and Its Origin for Enhancing CO_2 Affinity by Metal Substitution.* J. Phys. Chem. Lett. 3 (2012) pp. 826−829.

[45] J. L. C. Fajín, F. Illas, and J. R. B. Gomes, *Effect of the exchange-correlation potential and of surface relaxation on the description of the H2O dissociation on Cu(111).* J. Chem. Phys. 130 (2009) 224702-1:8.

[46] S. Grimme, Semiempirical *GGA-type density functional constructed with a long-range dispersion correction.* J. Comput. Chem. 27 (2006) pp. 1787-1799.

[47] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, *Van der Waals Density Functional for General Geometries.* Phys. Rev. Lett. 92 (2004) 246401-1:4.

[48] D. C. Langreth, B. I. Lundqvist, S. D. Chakarova-Käck, V. R. Cooper, M. Dion, P. Hyldgaard, A. Kelkkanen, J. Kleis, L. Kong, S. Li, P. G. Moses, E. Murray, A. Puzder, H. Rydberg, E. Schröder, and T Thonhauser, *A density functional for sparse matter.* J. Phys.: Condens. Matter 21 (2009) 084203-1:15.

[49] H. S. Koh, M. K. Rana, J. Hwang, and D. J. Siegel, *Thermodynamic screening of metal-substituted MOFs for carbon capture.* Phys. Chem. Chem. Phys. 15 (2013) pp. 4573-4581.

[50] R. Poloni, B. Smit, and J. B. Neaton, *CO_2 Capture by Metal−Organic Frameworks with van der Waals Density Functionals.* J. Phys. Chem. A 116 (2012) pp. 4957−4964.

[51] P. Canepa, N. Nijem, Y. J. Chabal, and T. Thonhauser, *Diffusion of Small Molecules in Metal Organic Framework Materials.* Phys. Rev. Lett. 110 (2013) 026102-1:5.

[52] L. Grajciar, O. Bludský, and P. Nachtigall, *Water Adsorption on Coordinatively Unsaturated Sites in CuBTC MOF.* J. Phys. Chem. Lett. 1 (2010) pp. 3354–3359.

[53] L. Grajciar, A. D. Wiersum, P. L. Llewellyn, J. –S. Chang, and P. Nachtigall, *Understanding CO_2 Adsorption in CuBTC MOF: Comparing Combined DFT-ab Initio Calculations with Microcalorimetry Experiments.* J. Phys. Chem. C 115 (2011) pp. 17925–17933.

[54] G. C. Shearer, V. Colombo, S. Chavan, E. Albanese, B. Civalleri, A. Maspero, and S. Bordiga, *Stability vs. reactivity: understanding the adsorption properties of $Ni_3(BTP)_2$ by experimental and computational methods.* Dalton Trans., 42 (2013) pp. 6450–6458.

[55] Y. Y. Sun, Y. –H. Kim, K. Lee, D. West, and S. B. Zhang, *Altering the spin state of transition metal centers in metal–organic frameworks by molecular hydrogen adsorption: a first-principles study.* Phys. Chem. Chem. Phys. 13 (2011) pp. 5042–5046.

[56] J. Sculley, D. Yuan, H. –C. Zhou, *The current status of hydrogen storage in metal–organic frameworks—updated.* Energy Environ. Sci. 4 (2011) pp. 2721-2735.

[57] Y. Liu, Z. U. Wang, H. –C. Zhou*, Recent advances in carbon dioxide capture with metal-organic frameworks.* Greenhouse Gases: Sci. Technol. 2 (2012) pp. 239–259.

[58] E. -Y. Choi, C. A. Wray, C. Hu, W. Choe, *Highly tunable metal–organic frameworks with open metal centers.* CrystEngComm 11 (2009) pp. 553-555.

[59] A. Mendiratta, C. C. Cummins, F. A. Cotton, S. A. Ibragimov, C. A. Murillo, and D. Villagrán, *A Diamagnetic Dititanium(III) Paddlewheel Complex with No Direct Metal−Metal Bond.* Inorg. Chem. 2006, 45 (2006) pp. 4328−4330.

[60] S. Bordiga, L. Regli, F. Bonino, E. Groppo, C. Lamberti, B. Xiao, P. S. Wheatley, R. E. Morris, and A. Zecchina, *Adsorption properties of HKUST-1 toward hydrogen and other small molecules monitored by IR.* Phys. Chem. Chem. Phys. 9 (2007) pp. 2676-2685.

[61] M. Fischer, J. R. B. Gomes, M. Fröba, and M. Jorge, *Modeling Adsorption in Metal–Organic Frameworks with Open Metal Sites: Propane/Propylene Separations*. *Langmuir* 28 (2012) pp 8537–8549.

[62] M. Kosa, M. Krack, A. K. Cheetham, and M. Parrinello, *Modeling the Hydrogen Storage Materials with Exposed M^{2+} Coordination Sites*.J.Phys. Chem. C. 112 (2008) pp. 16171–16173.

[63] M. Fischer, F. Hoffmann, and M. Fröba, *Molecular simulation of hydrogen adsorption in metal-organic frameworks.* Colloids Surf., A 357 (2010), pp. 35–42.

[64] M. Fischer, *Molecular Simulations of Hydrogen Storage and Gas Separation in Metal-Organic Frameworks*. Ph. D. Thesis, University of Hamburg, 2011.

[65] C. Hansch, A. Leo, and R. W. Taft, *A survey of Hammett substituent constants and resonance and field parameters*.Chem. Rev. 91 (1991) pp 165–195.

[66] F. Vermoortele, M. Vandichel, B. Van de Voorde, R. Ameloot, M. Waroquier, V. Van Speybroeck, and D. De Vos, *Electronic effects of linker substitution on Lewis acid catalysis with Metal-organic frameworks*. Angew.Chem. Int. Ed., 51 (2012) pp. 4887-4890.

[67] D. A. Gomez, and G. Sastre, *From microscopic insights of H_2 adsorption to uptake estimations in MOFs*. Phys. Chem. Chem. Phys. 13 (2011) 16558–16568.

[68] Y. -H. Kim, J. Kang, S. –H. Wei*, Origin of Enhanced Dihydrogen-Metal Interaction in Carboxylate Bridged Cu_2–Paddle-Wheel Frameworks*. Phys. Rev. Lett. 105 (2010) 236105-1:4.

[69] L. Ding, and A. O Yazaydin, *How Well Do Metal−Organic Frameworks Tolerate Flue Gas Impurities?*.J. Phys. Chem. C 116 (2012) pp. 22987−22991.

[70] J. Yu, Y. Ma, and P. B. Balbuena, *Evaluation of the Impact of H_2O, O_2, and SO_2 on Postcombustion CO_2 Capture in Metal−Organic Frameworks*. Langmuir 28 (2012) pp. 8064−8071.

[71] N. Nijem, P. Canepa, L. Kong, H. Wu, J. Li, T. Thonhauser, and Y. J Chabal, *Spectroscopic characterization of van der Waals interactions in a metal organic framework with unsaturated metal centers: MOF-74–Mg*. J. Phys.: Condens. Matter 24 (2012) pp. 424203-1:8.

[72] P. Verma, X. Xu, and D. G. Truhlar, *Adsorption on Fe-MOF-74 for C1-C3 Hydrocarbon Separation* J. Phys. Chem. C 117 (2013) pp 12648-12660.

[73] Q. Yang, and C. Zhong, *Understanding Hydrogen Adsorption in Metal-Organic Frameworks with Open Metal Sites: A Computational Study*. J. Phys. Chem. B 110 (2006) pp. 655-658.

[74] L. Kong, G. Román-Pérez, J. M. Soler, and D. C. Langreth, *Energetics and Dynamics of H_2 Adsorbed in a Nanoporous Material at Low Temperature*. Phys. Rev. Lett. 103 (2009) pp. 096103-1:4.

[75] Y. Liu, H. Kabbour, C. M. Brown, D. A. Neumann, C. C. Ahn, *Increasing the density of adsorbed hydrogen with coordinatively unsaturated metal centers in metal-organic frameworks.* Langmuir 24 (2008) pp. 4772-4777.

[76] R. Poloni, B. Smit, and J. B. Neaton, *Ligand-Assisted Enhancement of CO_2 Capture in Metal−Organic Frameworks*.J. Am. Chem. Soc. 134 (2012) pp. 6714−6719.

[77] G. E. Norman and V. S. Filinov, *Investigations of phase transitions by a Monte-Carlo method.* High Temp. 7 (1969), pp. 216-222.

[78] D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications*, 2nd ed.; Academic Press: San Diego, CA, 2002.

[79] A. L. Myers, and P. A. Monson, P. A., *Adsorption in porous materials at high pressure: Theory and experiment.*Langmuir 18 (2002), pp. 10261-10273.

[80] I. G. Kaplan, *Intermolecular Interactions: Physical Picture, Computational Methods and Model Potentials*, John Wiley & Sons Ltd., Chichester, UK, 2006.

[81] M. G. Martin and J. I. Siepmann, *Transferable potentials for phase equilibria. 1. United-atom description of n –alkanes.* J. Phys. Chem. B 102 (1998), pp. 2569-2577.

[82] A. K. Rappé, C. J. Casewit, K. S. Colwell, W. A. Goddard III, and W. M. Skiff, *UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations.* J. Am. Chem. Soc. 114 (1992), pp. 10024-10035.

[83] S. L. Mayo, B. D. Olafson, and W. A. Goddard III, *DREIDING: a generic force field for molecular simulations.* J. Phys. Chem. 94 (1990), pp. 8897-8909.

[84] W. L. Jorgensen and J. Tirado-Rives, *The OPLS Force Field for Proteins. Energy Minimizations for Crystals of Cyclic Peptides and Crambin.*J.Am. Chem. Soc. 110 (1988), pp.1657-1666.

[85] S. Keskin, J. Liu, R. B. Rankin, J. K. Johnson, and D. S. Sholl, *Progress, opportunities, and challenges for applying atomically detailed modeling to molecular adsorption and transport in metal−organic framework materials.* Ind. Eng. Chem. Res. 48 (2009), pp. 2355-2371.

[86] T. Düren, L. Sarkisov, O. M. Yaghi, R. Q. Snurr, *Design of new materials for methane storage.* Langmuir, 20 (2004), pp. 2683-2689.

[87] J. Perez-Pellitero, H. Amrouche, F. R. Siperstein, G. Pirngruber, C. Nieto-Draghi, G. Chaplais, A. Simon-Masseron, D. Bazer-Bachi, D. Peralta, and N. Bats, *Adsorption of CO_2, CH_4, and N_2 on ZeoliticImidazolate Frameworks: Experiments and Simulations.* Chem. Eur. J. 16 (2010), pp. 1560-1571.

[88] D. Fairen-Jimenez, R. Galvelis, A. Torrisi, A. D. Gellan, M. T. Wharmby, P. A. Wright, C. Mellot-Draznieks, N. A. Seaton, and T. Düren, *Swing Effect on the Adsorption of Energy-Related Gases on ZIF-8. A simulation and experimental approach.* Dalton Trans. 41 (2012), pp. 10752-10762.

[89] L. Chen, L. Grajciar, P. Nachtigall, and T. Düren, *Accurate Prediction of Methane Adsorption in a Metal-Organic Framework with Unsaturated Metal Sites by Direct*

Implementation of an ab Initio Derived Potential Energy Surface in GCMC Simulation. J. Phys. Chem. C 115 (2011), pp. 23074-23080.

[90] J. G. McDaniel and J. R. Schmidt, *Robust, Transferable, and Physically Motivated Force Fields for Gas Adsorption in Functionalized ZeoliticImidazolate Frameworks.* J. Phys. Chem. C 116 (2012), pp. 14031-14039.

[91] N. Lamia, M. Jorge, M. A. Granato, F. A. Almeida Paz, H. Chevreau, and A. E. Rodrigues, *Adsorption of propane, propylene and isobutane on a metal–organicframework: Molecular simulation and experiment.*Chem. Eng. Sci. 64 (2009), pp. 3246-3259.

[92] E. Garcia-Perez, J. Gascon, V. Morales-Florez, J. M. Castillo, F. Kapteijn, and S. Calero, *Identification of Adsorption Sites in Cu-BTC by Experimentation and Molecular Simulation.* Langmuir 25 (2009), pp. 1725-1731.

[93] J. Liu, J. T. Culp, S. Natesakhawat, B. C. Bockrath, B. Zande, S. G. Sankar, G. Garberoglio, and J. K. Johnson, *Experimental and Theoretical Studies of Gas Adsorption in Cu3(BTC)2: An Effective Activation Procedure.* J. Phys. Chem. C 111 (2007), pp. 9305-9313.

[94] J. Liu, R. Rankin, and J. K. Johnson, *The importance of charge-quadrupole interactions for H_2 adsorption and diffusion in CuBTC.*Mol.Simul., 35 (2009) pp. 60–69.

[95] M. Fischer, F. Hoffmann, and M. Fröba, *Preferred Hydrogen Adsorption Sites in Various MOFs – A Comparative Computational Study.*ChemPhysChem 10 (2009), pp. 2647–2657.

[96] A. Ö. Yazaydın, R. Q. Snurr, T.-H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low, and R. R. Willis, *Screening of metal-organic frameworks for carbon dioxide capture from flue gas using a combined experimental and modeling approach.* J. Am. Chem. Soc. 131 (2009), pp. 18198–18199.

[97] L. Hamon, N. Heymans, P. L. Llewellyn, V. Guillerm, A. Ghoufi, S. Vaesen, G. Maurin, C. Serre, G. De Weireld, and G. D. Pirngruber, *Separation of CO_2-CH_4 mixtures in the mesoporous MIL-100(Cr) MOF: experimental and modelling approaches.* Dalton Trans. 41 (2012), pp. 4052-4059.

[98] J. R. Karra, and K. S. Walton, *Effect of open metal sites on adsorption of polar and nonpolar molecules in metal-organic framework Cu-BTC.* Langmuir 24 (2008), pp. 8620–8626.

[99] M. Fischer, F. Hoffmann, and M. Fröba, *Metal–organic frameworks and related materials for hydrogen purification: Interplay of pore size and pore wall polarity,* RSC Adv. 2 (2012), pp.4382–4396.

[100] A. Martín-Calvo, F. D. Lahoz-Martín, and S. Calero, *Understanding Carbon Monoxide Capture Using Metal–Organic Frameworks,* J. Phys. Chem. C 116 (2012), pp. 6655-6663.

[101] J. M. Castillo, T. J. H. Vlugt, and S. Calero, *Understanding Water Adsorption in Cu−BTC Metal−Organic Frameworks.* J. Phys. Chem. C 112 (2008), pp. 15934–15939.

[102] C. Petit, L. Huang, J. Jagiello, J. Kenvin, K. E. Gubbins, and T. J. Bandosz, *Toward Understanding Reactive Adsorption of Ammonia on Cu-MOF/Graphite Oxide Nanocomposites.* Langmuir 27 (2011), pp. 13043–13051.

[103] M. Jorge, N. Lamia, and A. E. Rodrigues, *Molecular simulation of propane/propylene separation on the metal–organic framework CuBTC.* Colloids Surf., A 357 (2010) pp. 27–34.

[104] M. Jorge, M. Fischer, J. R. B. Gomes, C. Siquet, J. C. Santos, and A. E. Rodrigues, *Accurate model for predicting adsorption of olefins and paraffins on MOFs with open metal sites.*Submitted for publication.

[105] O. Engkvist, P.-O.Åstrand, and G. Karlström, *Accurate intermolecular potentials obtained from molecular wave funcions: Bridging the gap between quantum chemistry and molecular simulations.* Chem. Rev. 100 (2000), pp. 4087-4108.

[106] Z. Xiang, D. Cao, J. Lan, W. Wang, and D. P. Broom, *Multiscale simulation and modelling of adsorptive processes for energy gas storage and carbon dioxide capture in porous coordination frameworks.* Energy Environ. Sci. 3 (2010), pp. 1469–1487.

[107] H. Fang, P. Kamakoti, J. Zang, S. Cundy, C. Paur, P. I. Ravikovitch, and D. S. Sholl, *Prediction of CO_2 Adsorption Properties in Zeolites Using Force Fields Derived from Periodic Dispersion-Corrected DFT Calculations.*J. Phys. Chem. C 116 (2012), pp. 10692−10701.

[108] E. Klontzas, E. Tylianakis, and G. E. Froudakis, *Hydrogen Storage in 3D Covalent Organic Frameworks.AMultiscale Theoretical Investigation.* J. Phys. Chem. C 112 (2008), pp. 9095-9098.

[109] S. S. Han, H. Furukawa, O. M. Yaghi, and W. A. Goddard, III, *Covalent Organic Frameworks as Exceptional Hydrogen Storage Materials*.J. Am. Chem. Soc. 130 (2008), pp. 11580-11581.

[110] D. Cao, J. Lan, W. Wang, and B. Smit, *Lithium-Doped 3D Covalent Organic Frameworks: High-Capacity Hydrogen Storage Materials.*Angew. Chem., Int. Ed. 48 (2009), pp. 4730-4733.

[111] W. Li, S. Grimme, H. Krieg, J. Möllmann, and J. Zhang, *Accurate Computation of Gas Uptake in Microporous Organic Molecular Crystals.*J. Phys. Chem. C, 116 (2012), pp. 8865−8871.

[112] Z. Xiang, J. Lan, D. Cao, X. Shao, W. Wang, and D. P. Broom, *Hydrogen Storage in Mesoporous Coordination Frameworks: Experiment and Molecular Simulation.* J. Phys. Chem. C 113 (2009), pp. 15106-15109.

[113] J. Fu and H. Sun, *An Ab Initio Force Field for Predicting Hydrogen Storage in IRMOF Materials.* J. Phys. Chem. C 113 (2009), pp. 21815–21824.

[114] S. S. Han, W.-C. Deng, and W. A. Goddard, III, *Improved Designs of Metal–Organic Frameworks for Hydrogen Storage.*Angew. Chem., Int. Ed. 46 (2007), pp. 6289-6292.

[115] B. Assfour, S. Leoni, S. Yurchenko, and G. Seifert, *Hydrogen storage in zeolite imidazolateframeworks.Amultiscale theoretical investigation.* Int. J. Hydrogen Energy 36 (2011), pp. 6005-6013.

[116] R. B. Getman, Y.-S.Bae, C. E. Wilmer, and R. Q. Snurr, *Review and Analysis of Molecular Simulations of Methane, Hydrogen, and Acetylene Storage in Metal-Organic Frameworks.*Chem. Rev. 112 (2012), pp. 703–723.

[117] E. Tylianakis, E. Klontzas, and G. E. Froudakis, *Multi-scale theoretical investigation of hydrogen storage in covalent organic frameworks.*Nanoscale 3 (2011), pp. 856–869.

[118] S. S. Han, J. L. Mendoza-Cortes, and W. A. Goddard, III, *Recent advances on simulation and theory of hydrogen storage in metal–organic frameworks and covalent organic frameworks.* Chem. Soc. Rev. 38 (2009), pp. 1460–1476.

[119] L. Chen, C. A. Morrison, and T. Düren, *Improving Predictions of Gas Adsorption in Metal−Organic Frameworks with Coordinatively Unsaturated Metal Sites: Model Potentials, ab initio Parameterization, and GCMC Simulations.*J. Phys. Chem. C 116 (2012), pp. 18899−18909.

[120] A. L. Dzubak, L.-C. Lin, J. Kim, J. A. Swisher, R. Poloni, S. N. Maximoff, B. Smit, and L. Gagliardi, *Ab initio carbon capture in open-site metal–organic frameworks.* Nature Chem. 4 (2012), pp. 810-816.

[121] S. Grimme, *Semiempirical hybrid density functional with perturbative second-order correlation.* J. Chem. Phys. 124 (2006), pp. 034108.

[122] O. Bludský, M. Rubeš, P. Soldán, and P. Nachtigall, *Investigation of the benzene-dimer potential energy surface: DFT/CCSD(T) correction scheme.* J. Chem. Phys. 128 (2008), pp. 114102.

[123] M. Fischer, B. Kuchta, L. Firlej, F. Hoffmann, and M. Fröba, *Accurate Prediction of Hydrogen Adsorption in Metal−Organic Frameworks with Unsaturated Metal Sites via a Combined Density-Functional Theory and Molecular Mechanics Approach.* J. Phys. Chem. C 114 (2010), pp. 19116–19126.

[124] M. Fischer, F. Hoffmann, and M. Fröba, *New Microporous Materials for Acetylene Storage and C_2H_2/CO_2 Separation: Insights from Molecular Simulations.*ChemPhysChem 11 (2010), pp. 2220–2229.

[125] D. A. Gomez, A. F. Combariza, and G. Sastre, *Confinement effects in the hydrogen adsorption on paddle wheel containing metal-organic frameworks.* Phys. Chem. Chem. Phys. 14 (2012), pp. 2508–2517.

[126] J. Toda, M. Fischer, M. Jorge, and J. R. B. Gomes, *Water adsorption on a copper formate paddlewheel model of CuBTC: A comparative MP2 and DFT study.*Submitted for publication.

[127] C. Prosenjak, A.-M.Banu, A. D. Gellan, and T. Düren, *Hydrogen thermal desorption spectra: insights from molecular simulation.* Dalton Trans. 41 (2012), pp. 3974–3984.

[128] J. D. Weeks, D. Chandler, and H. C. Andersen, *Role of repulsive forces in determining the equilibrium structure of simple liquids.* J. Chem. Phys. 54 (1977), pp. 5237-5247.

[129] A. L. Myers and J. M. Prausnitz, *Thermodynamics of mixed-gas adsorption.*AIChE J.111 (1965),pp. 121-127.